A GEOCHEMICAL INVESTIGATION OF THE SEDIMENTS IN SMALL BAY, SALDANHA BAY, WITH SPECIAL REFERENCE TO THE MOBILITY OF Cd, Cu, Pb AND Zn.

DIANE LESLEY SCOTT
B.Sc. (Hons) (Chemistry) (UCT)

Submitted in partial fulfillment of the requirements of the degree of

MASTER OF SCIENCE IN ENVIRONMENTAL GEOCHEMISTRY

Department of Geological Sciences
University of Cape Town
March 1999

ACKNOWLEDGEMENTS

I would like to express my gratitude to the following for their contribution to this project:

Associate Professors James Willis and Martin Fey for their enthusiasm, advice and concern in all matters.

Dr Julius Pretorius (CSIR, Stellenbosch), for thought-provoking discussions on marine chemistry and guidance throughout the project.

Dr Pedro Monteiro (CSIR, Stellenbosch), for discussions on oceanographic matters.

Andy Pascall and Sebastian Brown (CSIR, Stellenbosch), for co-ordination of the laboratory analyses and for making my time spent at the CSIR a rewarding and enjoyable experience.

Khuthala Funani (CSIR, Stellenbosch), for invaluable assistance in the lab and for your lack of fear in getting muddy.

Associate Professor James Willis, Mrs Fran Pocock and Mr Ernest Stout (Department of Geological Sciences, UCT) for their assistance in the XRF analyses.

To Lisa Cavé and Christoff Soltau for providing comfortable accommodation in the Jonkershoek Valley for the period spent working at the CSIR.

Mike Louw (CSIR, Stellenbosch), for the analysis of DOC and the tour around the lab.

Dr Hartwig Frimmel and Dr John Rogers (Department of Geological Sciences, UCT) for advice on crystallographic matters and marine sediments, respectively.

Mr Neville Buchanan and Mr Ivan Wilson (Department of Geological Sciences, UCT), for their assistance in producing the final product.

Eskom, for their financial assistance.

The Environmental Geochemistry clan of 1998: Bernadette Azzie, Alex Campbell, Lisa Cavé, Portia Ceruti, Anja Gassner, Fiona McGregor, David Sugarman and Stewart Whyte, for their friendship and for adding much enjoyment to the year.....keep the lava flowing.

To the folks, Mike and Julie, for your support and patience during the year.

To Mac, for your remarkable ability to straighten the wheel, no matter how big the kink.

MATTERS PHILOSOPHICAL

Snow

The room was suddenly rich and the great bay-window was
Spawning snow and pink roses against it
Soundlessly collateral and incompatible:
World is suddener than we fancy it.

World is crazier and more of it than we think,
Incorrigibly plural. I peel and portion
A tangerine and spit the pips and feel
The drunkenness of things being various.

And the fire flames with a bubbling sound for world
Is more spiteful and gay than one supposes-
On the tongue on the eyes on the ears in the palms of one's hands-
There is more than glass between the snow and the huge roses.

Louis MacNeice

"A cloud does not know why it moves in just such a direction and at such a speed...it feels an impulsion...this is the place to go now. But the sky knows the reasons and the patterns behind all clouds, and you will know, too, when you lift yourself high enough to see beyond horizons"

Richard Bach (Illusions – the adventures of a reluctant Messiah)

Spirit

Man gets tired
Spirit don't
Man surrenders
Spirit won't
Man crawls
Spirit flies
Spirit lives when man dies

Man seems
Spirit is
Man dreams
Spirit lives
Man is tethered
Spirit free
What spirit is man can be

Mike Scott (This is the Sea)

ABSTRACT

Saldanha Bay is a natural deep-water harbour situated on the Cape West Coast, approximately 100 km north of Cape Town. The bay is not an estuary, since there are no rivers or streams entering the inlet. Saldanha Bay covers a total area of approximately 9.61 x 10^7 m^2 and consists of three interconnected water bodies: Langebaan Lagoon, Big Bay and Small Bay. The latter two are separated from each other by a causeway and a series of jetties. At present, Small Bay is the most developed of the water bodies, supporting activities such as commercial and industrial fishing, the mariculture of mussels, and the exportation of iron ore and metal concentrates. Conflicting demands are being placed on the system, and the sediments are known to be contaminated with a range of trace metals. The handling of ore and metal concentrates in particular, have been identified as a threat to the survival of the mariculture industries.

The overall objective of this study was to provide a geochemical characterisation of the sediments in Small Bay. It focused on identifying the factors which have the greatest influence on the mobilities of Cd, Cu, Pb *and* Zn *in the sediments. This was achieved through a geochemical interpretation of the results obtained from analyses of sediment solid phase samples and pore water samples. Factors affecting the metal mobilities were identified by investigating the statistical relationships between calculated partition coefficients* (K_p) *and the characteristics of the sediment solid and aqueous phases.*

Sediment core samples were taken at strategic locations in Small Bay. Interstitial waters were obtained by compressing the sediments in gas-operated squeezers. The following laboratory analyses were performed on the sediment solid phase: acid volatile sulfide (AVS) content and simultaneously extracted metals (SEM); organic C, N *and* H, *organic carbon content of extracted humic and fulvic acids; concentrations of amorphous oxyhydroxides; total element concentrations of major and trace elements and concentrations of readily available metals. Mineralogical analyses were performed on selected clay fractions. The concentrations of the*

readily available metals were used to calculate partition coefficients. The following analyses were performed on the pore waters: pH, EC, alkalinity, major cations and anions, dissolved NH_3-N, *dissolved* PO_4-P, *DOC and trace metals.*

The sediments of Small Bay are highly variable with respect to sulfide content, organic matter content, major element concentrations as well as trace metal concentrations. The sediments are generally anoxic and AVS concentrations range from 61-8906 μmol/kg.

The range of organic carbon concentrations (0.3 to 7.0 %) is fairly typical of nearshore sediments. A broad range of C/N *ratios (0.62 to 35) may be due to varying degrees of both bioturbation and resuspension of organic material in the bay.*

Given the anoxic nature of the sediments, it is doubtful whether the concentrations of Fe *and* Mn *in the extraction of oxyhydroxides provide a true reflection of the quantities of reducible iron and manganese in the sediments. Most of the* Fe *and* Mn *is likely to be associated with sulfides.*

Mica (probably illite), kaolinite, quartz, plagioclase feldspars, aragonite, calcite and undifferentiated 2: 1 layer silicates have been found in some or all of the clay fractions. Of these components, the undifferentiated 2:1 layer silicates would be the minerals most likely to contribute to the cation exchange capacity of the sediment solid phase.

The sediments are composed mainly of SiO_2 *and* $CaCO_3$. *Very high trace metal concentrations have been detected but these are localised within the bay. Average concentrations (outliers excluded) of* Cd, Cu, Pb *and* Zn *have all increased slightly over the past 15 years. Cadmium concentrations in the sediment solid phase range from 0.55 to 2.31 mg/kg. Copper concentrations range from about 5 to 143 mg/kg. Solid phase lead concentrations range from less than 4.6 mg/kg to 287 mg/kg. Levels of zinc in the solid phase range from 10 to 279 mg/kg.*
All the pore water samples are more saline than typical seawater. Electrical conductivities range from 44 to 54 mS/cm. The pH of the interstitial waters is

alkaline and ranges from 7.7 to 8.5. Alkalinity demonstrates considerable spatial variation. Concentrations of HCO_3^- *range from 230 to 948 mg/L and all pore water samples have higher alkalinity than typical seawater (107 mg/L).*

Nitrogen concentrations (detected as ammonia) range from 18 to 99 mg/L. These levels greatly exceed the range of NH_3–N *concentrations in typical seawater. The high ammonia concentrations reflect the anoxic state of the interstitial waters.*

Phosphorus (detected as phosphate) in the pore waters ranges from <0.01 to 18 mg/L. Five of the 13 pore water samples have PO_4-P *concentrations which are roughly two orders of magnitude greater than the upper limit of the typical seawater range. Variation in* PO_4-P *concentrations is probably related to the differences in localised quantities of organic matter in the sediments.*

Pore water concentrations of cadmium (0.07-2.64 μg/L), copper (0.39-65.9 μg/L) and zinc (1.91-130 μg/L) span a two-order of magnitude range. Levels of lead in the pore waters range from 1.00 to 17.8 μg/L.

By relating the calculated partition coefficients to selected variables, it was concluded that cadmium mobility appears to increase by the formation of soluble phosphate, carbonate and organic species. Mobility is reduced by the formation of insoluble Cd-*sulfides. Like cadmium, the mobility of copper is increased by the formation of carbonate, phosphate and organic species. Copper mobility may also be reduced by the formation of sulfides. The mobility of lead is limited in sediments by the formation of sulfides. It is indicated, that lead mobility may be facilitated by the formation of soluble lead phosphate. Zinc in the sediment solid phase does not appear to be strongly associated with sulfide content. The mobility of* Zn, *however, is increased, by the formation of soluble* Zn-*phosphate complexes.*

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS AND ACRONYMS

AVS	Acid volatile sulfides
COD	Chemical oxygen demand
CSIR	Council for Scientific and Industrial Research
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DON	Dissolved organic nitrogen
DOP	Dissolved organic phosphorus
EC	Electrical conductivity
FAAS	Flame atomic absorption spectrophotometry
GCQ	General cargo quay
HSAB	Hard soft Lewis acid-base principle
IUPAC	International Union of Pure and Applied Chemistry
K_p	Partition coefficient
K_{sp}	Solubility product
LOI	Loss on ignition
OA	Oxygen available
PCA	Principal component analysis
POC	Particulate organic carbon
POM	Particulate organic matter
PON	Particulate organic nitrogen
POP	Particulate organic phosphate
RSD	Relative standard deviation
SEM	Simultaneously extractable metals
SFRI	Sea Fisheries Research Institute
WDXRFS	Wavelength dispersive X-ray fluoresence spectrometry
XRD	X-ray diffraction
XRF	X-ray fluoresence

CHAPTER 1

Introduction

1.1 General background

Saldanha Bay is situated on the Cape West Coast, approximately 100 km north of Cape Town (Figure 1.1). This coastal inlet is named after the famous Portuguese navigator Antonio de Saldanha who stopped in Southern Africa in 1503 on his way to the east. Early European settlers were attracted to the area by the sheltered waters and the strategic location of the Bay, and it quickly developed into an important trading centre. Today, Saldanha Bay provides the only harbour on the West Coast which is naturally well protected from the prevailing winds and from the heavy swells that can occur during winter storms (CSIR, 1995).

Whilst the Bay is influenced by tides, it is not an estuary since there are no perennial streams or rivers entering the inlet. Saldanha Bay includes a group of interconnected water bodies consisting of Small Bay, which is north-west of the iron ore causeway (Figure 1.2) and Big Bay, which extends into Langebaan Lagoon, south-east of the causeway. The 16 km long Lagoon is shallow and contains salt marshes, tidal flats and tidal channels (de la Cruz, 1978). The total area of Saldanha Bay is estimated at $9.61 \times 10^7 m^2$. Of this Small Bay comprises $1.41 \times 10^7 m^2$ and Big Bay $4.31 \times 10^7 m^2$ (Carter, 1995).

The features of Saldanha Bay make it suitable for a range of beneficial but possibly conflicting uses. These include,

- protection from the high energy coastline;
- being influenced with the nutrient rich and productive southern Benguela upwelling system;
- close proximity to fishing grounds;
- being a deep water bay with no river inflows which could cause siltation;
- a pristine marine reserve in the lagoon system which has the highest invertebrate species diversity in the South African coast zone (CSIR, 1995).

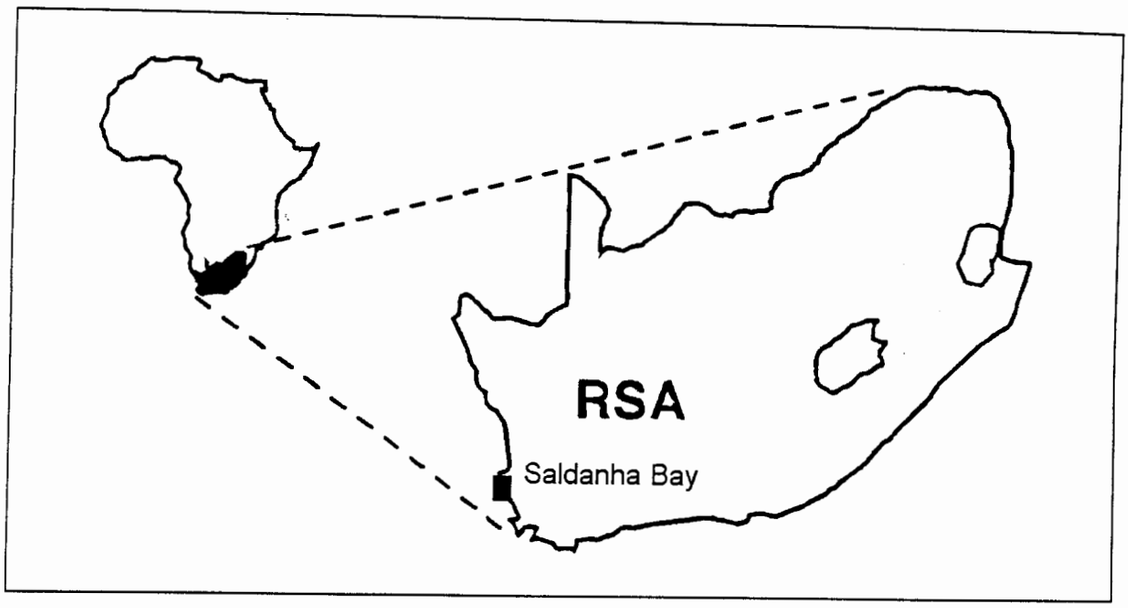


Figure 1.1 Location of Saldanha Bay in South Africa.

At present, Small Bay is the most developed area of Saldanha Bay, supporting activities such as,

- shipping and industrial trading of manufactured goods and raw materials (including iron ore and concentrates of copper, lead and zinc)
- fishing and fish processing
- mariculture (particularly mussel mariculture)
- collection of beach cast seaweeds
- tourism and recreation (CSIR, 1995)

Given that the uses of Saldanha Bay (particularly Small Bay) are so diverse, it is likely that the needs of these activities will come into conflict with one another. Of particular concern and interest, is the fate of trace metals in the sediment system. Considering that large quantities of metal ore are being handled in the Bay, the fact that aquatic sediments tend to accumulate trace metals bears great significance on the environmental quality of the system.

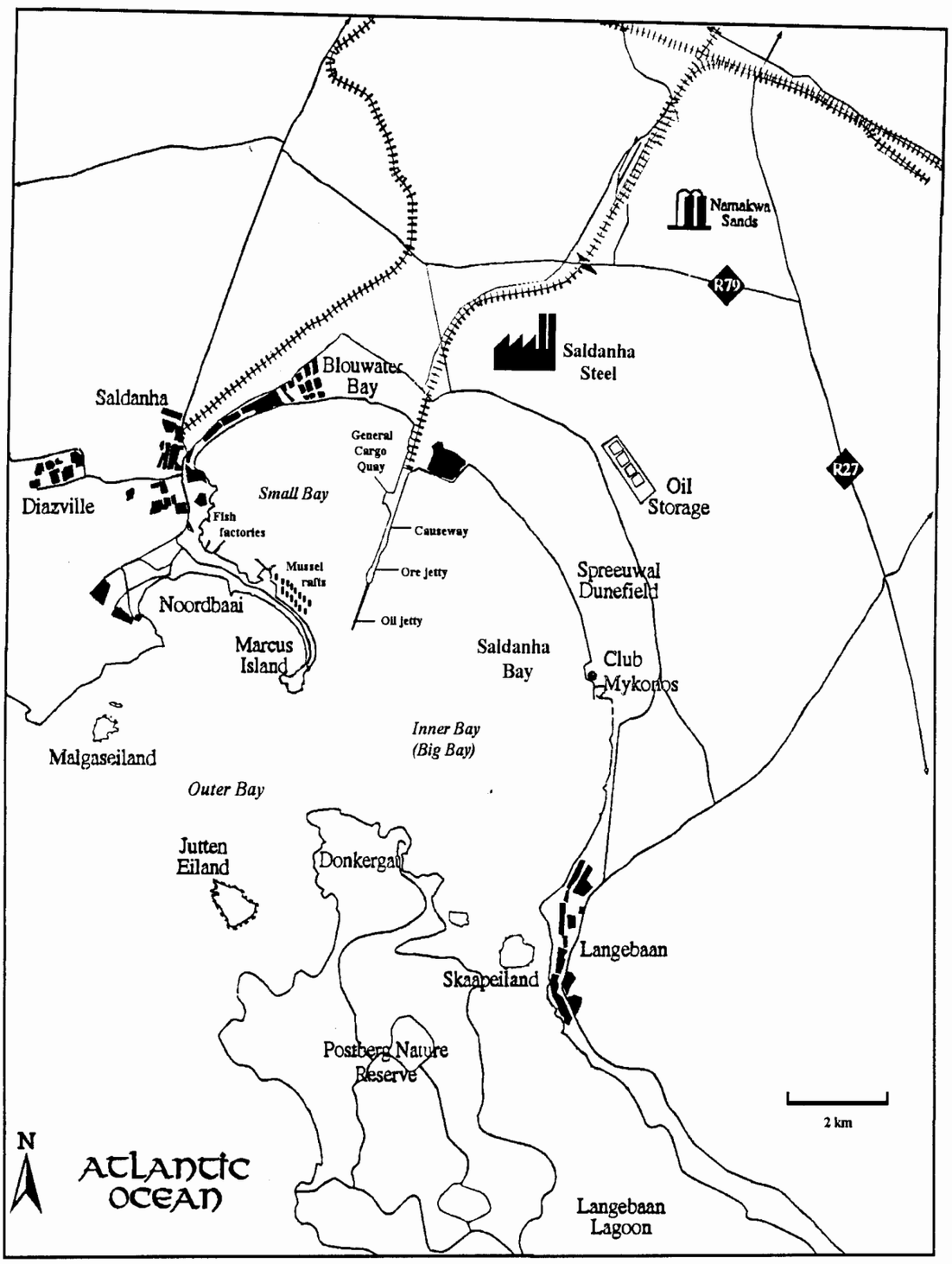


Figure 1.2 Map of the Saldanha Bay area showing Small Bay, Big Bay and Langebaan Lagoon (Adapted from CSIR, 1995).

1.2 Past and present industrial activity in the area

Shortly after Free Burghers from the Cape Colony established a settlement in Saldanha in 1658, industrial activity commenced in the area. The primary industries were sealing, seabird egg collection, whaling, fishing and agriculture (CSIR, 1995).

Industrial activity was based mainly on seal hunting until the 1840's, when large scale guano collecting began on the islands in the Bay. During the late 19th century the harvesting of penguin eggs and whaling flourished. In 1913 a railway was built to Saldanha Bay, encouraging industrial development, particularly in the form of phosphate exports and the development of the fishing industry. The fishing industry has been the largest provider of employment in the area, especially since the establishment of the deep-sea trawling industry in the 1950's (CSIR, 1995).

The late 1970's saw the arrival of iron ore exportation, oil transfer and storage facilities, all of which had a limited effect on development. A beach breakwater was constructed, extending about 2 km to Marcus Island to provide shelter from the waves (Theron, 1995). Jetties (extending 4 km offshore) were built for the loading of oil and iron ore. It was the construction of the General Cargo Quay (GCQ) in 1980, however, that allowed for the handling of a wider variety of cargo, including exports of lead, zinc and copper concentrates. Rail transport was improved with the completion of the Sishen-Saldanha railway line.

Further development came in the form of mariculture industries which established themselves in the Saldanha Bay area. Development during the rest of the 1980's was fairly stagnant. The 1990's have seen the establishment of the Namakwa Sands Smelter and the Saldanha Steel plant (CSIR, 1995).

Saldanha Bay harbour currently handles significant exports of iron ore and other partially processed metals, most of which are in the form of fine grains. Iron ore exports were approximately 19 million tons in 1994 and 21 million in 1995 (CSIR, 1995). Similar quantities of other ores were also exported during these periods (although zinc concentrate exports through Saldanha Bay ceased at the end of 1994) (CSIR, 1995).

Iron ore is tipped from train trucks and either moved to a stockpile for storage or transported directly to the ships on conveyor belts, from which it is emptied into the ship holds through a tube. The metal concentrates are stored in bulk and front-end loaders are used to move the material into bottom-opening skips, which dump the material into ship holds. Products from Namakwa Sands (which include materials from the Namakwa Sands Mine and Smelter, including, zircon, rutile, titanium slag and pig iron) are loaded into bottom-opening skips from silos and emptied directly into ship holds (CSIR, 1995).

1.3 Future industrial activity

It is expected that there will be a significant increase in small craft activities in Saldanha Bay which may come into conflict with the continuing industrial development (CSIR, 1995). It is predicted that the recent construction of the Saldanha Steel plant will encourage the establishment of secondary industries in the area. In terms of increased ore exports, it is likely that zinc concentrate exports will recommence in the near future (Theron, 1995).

There is considerable concern regarding the compatibility of the expanding Port of Saldanha and the plans to further develop the mariculture industry. At present, 200 people are employed by the mariculture industry in Small Bay which produces 2500-3000 tons of mussels annually. In the short term (1-3 years), this production is likely to double. It is estimated that, by extending the industry into Big Bay, total mussel production would be about 87000-107000 tons per annum, providing employment for 5000-8000 people (CSIR, 1995).

1.4 Previous studies in the area

To date, numerous studies have been conducted in Saldanha Bay. The majority of these have been baseline studies that were carried out before the construction of the ore jetty and GCQ, and specialist studies to determine the effects of further harbour expansion or industrial development on particular aspects of the Bay, such

as the mariculture and beaches. Programmes are currently in operation to monitor the levels of heavy metals in the sediments and in the mussels.

A short review of relevant, previous studies in the area is given below. A number of projects (which are not discussed here) have focused on the geology or marine flora and fauna of the area, and are not relevant to the focus of this study.

In April 1974 the Sea Fisheries branch of the Department of Industries started a detailed survey of the physical and chemical characteristics of the water in Saldanha Bay and Langebaan Lagoon, to establish baseline conditions in the area prior to the development of the Bay as a major port and industrial centre (Shannon and Stander, 1977). Water samples were collected at various depths from 18 stations on a quarterly basis. A variety of parameters were determined including, dissolved oxygen, nitrate, nitrite, inorganic phosphorus, total phosphorus, reactive silica, pH, chemical oxygen demand (COD) and oxygen absorbed. Heavy metal concentrations in marine organisms were also measured.

Shannon and Stander (1977) describe the state of the Bay at the time of writing (May 1977) as being relatively unpolluted. Appendix A contains the chemical and physical properties of the seawater at various depths for the 18 sites in Saldanha Bay (April 1974 to October 1975). Prior to 1974, organic pollution from the fish factories in Hoedjies Bay (the north-western corner of what is now called Small Bay) was serious but improved considerably following the installation of dry off-loading systems for the fish, early in 1974 (Shannon and Stander, 1977). The dissolved oxygen content in the Bay and Lagoon showed variations typical of a highly productive west coast marine environment. The pH of the water was generally high (surface water values sometimes being in excess of 8.4) and there was usually a decrease in pH with depth. It was suggested that the high pH readings may have been influenced by the primary production in the system (Shannon and Stander, 1977).

The geochemistry of Saldanha Bay sediments was investigated in 1977 by Willis *et al.* (1977). The study was part of a programme of chemical research co-ordinated by the Department of Planning and the Environment, and was designed to investigate as well

as monitor pollution in the area. Concern about pollution was prompted by plans for the export of iron ore from one of the harbours in the Bay. The main focus of this study was on the sediments in Langebaan Lagoon which are derived from wind-borne dust, erosion and material brought in from the sea by tidal currents. Concurrent with the work carried out by Willis *et al.* (1977), a study was conducted by Flemming (1977) on the sedimentology of the Bay. These two projects together provided a baseline for monitoring changes in the Saldanha Bay system.

Willis *et al.* (1977) found that the recent sediments in Saldanha Bay were very variable in composition: large concentration ranges were discovered for both SiO_2 (7.5-96.0 %) and $CaCO_3$ (1.3-88.8 %) and the sum of these two components was never less than 93 %. Mineralogically, the sediments were a three-component mixture of quartz, calcite and a granitic fraction presumed to be derived from granitic rock. Major element data are presented in Table 1.1.

Table 1.1 Average concentrations of major elements in the sediments of Saldanha Bay (n=21) determined by XRF spectrometry (Willis *et al.*, 1977).

Element	Concentration (%)
SiO_2	56.98
TiO_2	0.11
Al_2O_3	2.02
Fe_2O_3	0.36
MnO	0.003
MgO	0.42
CaO	20.92
Na_2O	0.56
K_2O	0.89
P_2O_5	0.48
S	0.25
H_2O	1.04
CO_2	16.42
Totals	100.33

CO_2 values were calculated assuming all CaO was present as calcium carbonate.

XRD (X-ray diffraction) analysis indicated that the sediments were composed predominantly of the three minerals: calcite, quartz and feldspar. Small amounts of aragonite were sometimes detected. It was found that the sediments contained almost no clay minerals. The mineralogy of the different size fractions was not fully determined, but it was suggested that the coarser fractions consisted mainly of calcite, while the finer fractions were composed mainly of quartz. Trace element data are presented in Table 1.2.

Table 1.2 Average concentrations of trace elements in the sediments of Saldanha Bay (n=21) determined by XRF spectrometry (Willis *et al.*, 1977).

Element	Concentration (ppm)
Ba	142
Sr	884
Rb	34
Y	14
Zr	145
Nb	~2
Zn	7
Cu	<1
Ni	<2
Co	<3
Cr	17
V	8
Br	22

Sediment samples collected from the sheltered western side of Saldanha Bay where the wave energy is low and where fine and very fine sand fractions predominate, were found by Willis *et al.* (1977) to have high SiO_2 and low $CaCO_3$ content. High concentrations of Sr, which substitutes for Ca in calcite, were found in the Bay. Levels of Cu, Ni and Co were below detection limits. Zirconium was high in the Bay sediments. Elevated Br levels were associated with high organic content. Analyses of chemical data for Saldanha Bay and Langebaan Lagoon revealed a strong negative

correlation between Sr and SiO_2 and a strong positive correlation between CaO and Sr. It was discovered that Al_2O_3 was strongly correlated with Fe_2O_3, Na_2O, K_2O, Ba and Rb; Fe_2O_3 with Na_2O and Rb; and Na_2O with K_2O, Ba and Rb. Strong correlations between K_2O and Ba as well as Rb were attributed to the fact that these elements commonly occur in the same minerals.

Gardner *et al.* (1985) report that shortly after the shipment of lead and copper concentrates from Saldanha Bay began in February 1980, the Sea Fisheries Research Institute (SFRI) designed pollution monitoring surveys to monitor certain types of pollution in the Bay. There were particular concerns about pollution from the shipment of iron ore and metal concentrates from the jetty and GCQ, fishing and the fish processing plants, and the oil jetty. The quarterly surveys involved taking sediment samples and collecting mussels and oysters for analysis. Samples of surface sediments were collected on each survey from between 12 and 14 sites within the Bay (Inner Bay, Outer Bay and Langebaan Lagoon). The results for the period 1980-1983 are presented as arithmetic means in Table 1.3.

Table 1.3 Annual mean concentrations (ppm, dry weight) of metals in Saldanha Bay sediments from 1980 to 1983 (Gardner *et al.*,1985).

	Cu	Fe	Zn	Mn	Pb	Cd
1980*	0.9 (11)	2120 (11)	12 (11)	12 (11)	1.5 (11)	0.2 (11)
1981	2.9 (55)	2240 (55)	10 (55)	17 (55)	2.6 (18)	0.3 (55)
1982	2.4 (48)	2740 (48)	13 (48)	18 (48)	2.7 (48)	0.2 (48)
1983	3.8 (56)	2230 (56)	15 (56)	19 (56)	5.8 (56)	0.4 (56)

*Single survey. Number of determinations given in parentheses.

Copper, zinc, lead and manganese increased over the period 1980-1983. The increases were attributed to data obtained from positions close to the GCQ (during 1982 and 1983) where levels of copper, iron, and lead were known to be high. Metal concentrations were found to be low compared to those of other South African harbours such as Durban, Port Elizabeth and Richards Bay, and were approximately half the levels found in the Knysna surface sediments (Gardner *et al.* 1985). High levels of copper and lead were occasionally found close to the GCQ but these were

the result of identifiable operational spills and not due to continuous accumulation. Gardner *et al.* (1985) concluded that metal concentrations in the sediments were low and that the GCQ operations had had little impact on the environmental quality of the Bay.

Carter (1995) investigated the proposals for the extension of the GCQ in Saldanha, which has required dredging of a section of the Bay to deepen and widen the ship navigation channels and turning circle. The dredging, which took place in 1997 (pers. com., P. Monteiro), removed approximately two million cubic meters of sediment, most of which is to be used as backfill for the GCQ extension.

Trace metal analyses performed by PORTNET and SFRI show that the sediments in the dredge area are contaminated. The total dredge area was divided into six zones. The average concentration of Fe detected in one of the six zones was 5900 mg/kg and the average concentrations of Pb, Zn and Cu in another zone were 465, 175 and 54 mg/kg respectively (Carter, 1995). The metal concentrations are similar to those of polluted sediments in major industrial ports and estuaries (Carter, 1995). Contamination has been attributed to spillage and dusts arising from shipments of iron ore, copper, lead, and to a lesser extent zinc, from the existing GCQ. During 1994/1995, 21 million tons of iron ore were exported from Saldanha Bay (Carter, 1995).

1.5 Study motivation and aims

Since the survival of the Saldanha Bay mariculture industries depends enormously on the environmental health of the Bay, programmes for monitoring the levels of heavy metals in the sediments and mussels are fully warranted. However, due to the fact that the fate of trace metals in a sediment system depends largely on the chemical and mineralogical composition thereof, it is vitally important to have an in-depth geochemical description of the sediments. This will allow for an accurate assessment of the behaviour of certain metals in the system and will make it easier to gauge how well buffered the Bay is against contamination inputs.

In this study, focus is placed on the mobility of cadmium, copper, lead and zinc in the sediments of Small Bay, Saldanha Bay. Each one of these metals represents a significant health hazard when present at an elevated concentration (Förstner and Wittmann, 1979; McBride, 1994).

The aims of this study are to answer certain key questions about the geochemistry of the sediments in Small Bay. These questions are:

1. What are the concentrations of Cd, Cu, Pb and Zn in the sediments and how are these elements distributed?
2. To what extent are the sediments being contaminated with these metals?
3. What factors control the mobility of these metals in the sediments?

The approach of this study has been to assess the extent of metal contamination in the Bay before deciding which factors have the greatest influence on the mobility of Cd, Cu, Pb and Zn in the sediments. Evaluation of the analytical data obtained during the course of the investigation will show how metal concentrations vary within the Bay, thus providing an answer to question number one.

In order to address the second question, concentrations of metals detected in the sediments during this project have been compared with those found in previous studies. Baseline studies conducted prior to the construction of the ore jetty have been particularly significant. Data collected during monitoring programmes have also been valuable.

The main focus of this study is answering question three: a task which makes use of the equilibrium partitioning concept (described in section 2.7). Statistical relationships between the solid and solution phase properties, and the partition coefficients are sought.

Although attention is concentrated on specific areas of Small Bay that are viewed as being likely to have elevated metal levels, the distribution of sampling sites is extensive enough to address the spatial variation in heavy metal concentrations.

1.6 Further description of the study area

Certain aspects of the Saldanha Bay area are discussed further in this section.

1.6.1 Climate

The climate in the region of Saldanha Bay is semi-arid mediterranean with rainfall being restricted to the winter months (June-July). Summers are hot and dry, but slightly tempered by the proximity of the sea. The average temperature in summer is 21 °C and 10 °C during winter. Rainfall usually occurs in short bursts and reaches maximum levels of 50 mm/month during May, June and July and lowest levels of 10 mm/month during November through to March (Flemming, 1977). The long-term yearly average amounts to about 300 mm. There is very limited drainage in the immediate area of Saldanha Bay and there is no significant freshwater inflow to the Bay arising from surface runoff. This is significant when considering the origin of the nearshore sediments. There is no noteworthy supply of modern terrigenous material to the Bay and therefore the sediments are predominantly of coastal-marine origin (Flemming, 1977).

The most dominant wind component is formed by the south-westerly winds which are a local derivative of the Cape south-easters that blow persistently during the summer months (September – April). These winds are often strong, reaching 25 km/hour for over 90 days/year, although they rarely reach gale force (CSIR, 1995). The south westerlies play a large role in evaporation in the area as well as in the distribution of the coastal dunes. During the winter period, wind patterns are more variable (Flemming, 1977) and bergwinds occur more than 15 % of the time, reaching speeds of more than 30 km/hour (CSIR, 1995).

1.6.2 Geology

The landscape in the Saldanha Bay area is characterised by a gently undulating plain with low hills. The highest point is Postberg (192.8 m) on the Langebaan Peninsula.

There are no outstanding physical features except for occasional outcrops of granite boulders (CSIR, 1995).

The granites are members of the "Cape Granites" which occur in the south western Cape. Most of the granite in the Saldanha area is formed by the Hoedjiespunt granite and the Saldanha Quartz Porphyry. These are part of the Vredenburg pluton. The Hoedjiespunt granite is similar to the granite of the Cape Peninsula and is characterised by large feldspars phenocrysts (up to 5 cm in length) which are irregularly distributed in an abundance of biotite (de la Cruz, 1978).

The shores of Outer Bay possess outcrops of Saldanha Quartz Porphyry. This granite has minor phenocrysts of quartz, feldspars and biotite (de la Cruz, 1978). An extensive low plain has developed in the less resistant Malmesbury metamorphic rocks between the coastal area and the mountain ranges further afield. Tertiary to Recent sediments have been deposited on this plain. Large and diverse Pliocene fossil deposits have been discovered in the region. These include marine and terrestrial deposits (Flemming, 1977).

1.6.3 Morphology and hydrology

The coastline in the Saldanha area is marked with long sandy beaches and a few small rocky headlands. Water depth in Outer Bay ranges from 25 to 50 m and the Inner Bay depth range is 0 to 25 m, but the largest part of this area is between 5 and 15 m deep (Theron, 1995).

Saldanha Bay is open to the Atlantic Ocean near its northern end. The entrance was about 4.6 km across with the Marcus and Malgas islands on the north side and Jutten Island on the south. However, the construction of the breakwater and the causeway during the development of the Bay for iron ore export has closed off the northern section of the Bay and altered the connection to the ocean. The entrance to the Bay is now only 2.4 km wide (CSIR, 1995). The long-term effects of the breakwater and the causeway on the marine system have not been fully investigated. It has been found, however, that the water in Inner Bay is warmer than that of Outer Bay and the former

frequently has an oxygen deficit in the bottom waters, suggesting that there is limited circulation. There have also been changes in the bottom-dwelling fauna in Inner Bay which are attributed mainly to the large amount of organic matter entering the Bay from the fishing factories and the mussel beds. The poor circulation may be a contributing factor (CSIR, 1995).

Circulation patterns in both Small Bay and Big Bay differ in summer and winter because of thermal stratification during the summer period. The thermal gradient is caused by the presence of cold bottom water due to the Benguela upwelling system, which is associated with southerly and south-easterly winds. The upwelling brings cool, deep water of high biological productivity to the surface and this plays an important role in the deposition of organic sediments in the shallow environments (de la Cruz, 1978).

Water currents are predominantly controlled by wind. This applies particularly to surface currents, and less to bottom water currents, which don't always flow in the same direction as the wind (CSIR, 1995). Current speeds in Saldanha Bay are generally low. The velocities in Small Bay range from 4 to 21 cm/s, with an average of 12 cm/s. In a separate investigation, current speeds between 9 and 19 cm/s were measured for the shallow waters of Small Bay. Surface water flow in Small Bay is usually in a clockwise direction, with strong acceleration south-westwards down the iron-ore causeway. Cool water entering the Bay along the Marcus Island causeway will warm up as it moves around the Bay (CSIR, 1995).

Water exchange between the Bay and the ocean appears to be facilitated only during the summer upwelling season, when the process will occur at 6-12 day intervals. In winter water may be forced to leave Small Bay by very strong north and north-westerly winds. In such cases, bottom water will move in to replace it (CSIR, 1995).

Prior to the separation of Small Bay and Big Bay, the temperature of the water in Saldanha Bay averaged 10 °C in winter and 20 °C in summer. Salinity levels were similar to those of the open ocean, during both summer and winter. Average salinity in the Bay was about 34.9 ‰ but in summer a plume of slightly more saline water

(>35 ‰) was observed in the south-eastern part of Saldanha Bay (part of what is now called Big Bay), due to the influx of lagoon water during the ebb tide cycle (de la Cruz, 1978).

CHAPTER 2

The mobility of Cd, Cu, Pb and Zn in nearshore sediments
A literature review

2.1 Introduction

It has been well established that the fate of trace metals in natural systems not only depends on the absolute concentrations of the metals, but also on the chemical interactions which they undergo in different environments (Förstner and Wittmann, 1979; Shea, 1988; Morrison *et al.*, 1989; Burton and Statham, 1990; McBride, 1994; Drever, 1997). Metals entering a sediment system will partition between different components: a portion will associate with dissolved organic and inorganic ligands in the solution phase and another portion will interact with particulate matter, taking part in adsorption, precipitation or co-precipitation reactions. Trace metals compete with major cations for binding sites on particle surfaces (Clegg and Sarmiento, 1989). A significant amount of the metal may be utilised by plants and organisms. Ultimately, sediments are media that will accumulate trace metals and greatly influence their bioavailability. The concentrations of trace metals in sediments are, typically, orders of magnitude greater than those in the overlying water or interstitial water (Tessier and Campbell, 1988).

The purpose of this literature review is to detail the different types of metal-sediment interactions that have been identified in previous studies as having a significant influence on the mobility of trace metals in sediment systems. The emphasis of this review is on the behaviour of Cd, Cu, Pb and Zn in sediments and the partitioning of these metals between the sediment solid and solution phases.

2.2 Definitions of heavy metals and trace metals

The terms 'heavy metals' and 'trace metals' are often used without strict definition (Furness and Rainbow, 1990) and the interpretation of these terms usually depends on the context in which they are used. The term 'heavy metal' has been used as a

convenience to refer to metals which are potentially toxic (e.g. cadmium, mercury, lead and bismuth) (Alloway, 1995a). According to Förstner and Wittmann (1979), metals with an atomic mass greater than that of calcium are included in the heavy metal category.

Generally, the term trace metal is used to describe metals which are present in low concentrations in biological systems. Heavy metals are often referred to as trace metals because they fit this description, although the term trace metal can imply that the element is essential to organisms (Förstner and Wittmann, 1979). Many metals are essential to living organisms, but of these, the major metals sodium, potassium, calcium and magnesium are not considered to be heavy metals by any definition. Other metals which are essential to some organisms in trace quantities include aluminium, copper, iron, manganese, nickel, selenium, molybdenum, tin, vanadium, zinc, arsenic and chromium (Furness and Rainbow, 1990). Aluminium is excluded from most definitions of heavy metals, and the classifications of arsenic and selenium are more varied. The remaining essential trace metals however, are described as heavy metals. Non-essential heavy metals usually include cadmium, gold, lead, mercury and silver (Furness and Rainbow, 1990).

For practical purposes, the terms 'trace metals' and 'heavy metals' will be used synonymously, and in most cases will refer specifically to cadmium, copper, lead and zinc.

2.3 Characteristics of nearshore sediments

Nearshore sediments are deposited on the margins of the continents under a range of conditions. These conditions are greatly influenced by the adjacent land. The sediments include gravels, sands, silts and muds. Sand is the most common continental shelf sediment and can include biogenic sand, quartz (SiO_2) and glauconite ($K_{15}(Fe,Mg,Al)_{4-6}(Si,Al)_8O_{20}(OH)_4$) (King, 1974). Coastal sediments are composed of mixtures of terrigenous, authigenic and biogenous material. The biogenous component consists mainly of shell material (Chester, 1990). Nearshore sediments usually contain about 1-5 % organic carbon, but large amounts of organic

matter are found in areas of high primary production. For example, the organic-rich diatomaceous muds off the coast of Namibia contain up to about 25 % organic carbon (Chester, 1990). Coastal sediments typically accumulate at a relatively fast rate and become anoxic at shallow depths. The beige-brown oxic layer is usually no more than a few centimetres thick, and the sediments below are often conducive to the reduction of sulfate (Yen and Tang, 1977).

The major element composition of sediments depends largely on the relative proportions of the minerals. The dominant minerals are the clays (e.g. kaolinite and chlorite), biogenous carbonates (e.g. calcite) and opal (amorphous silica). Aluminium is concentrated in the clays, calcium in the carbonates and silicon in the siliceous ooze (Chester, 1990). Both oxic and anoxic coastal sediments can contain a range of authigenic minerals. These include iron sulfides, various carbonates (including those of iron and manganese) and iron and manganese oxyhydroxides (the term oxyhydroxide refers to hydroxides and hydrous oxides in general). Coastal sediments can contain a range of grain sizes: fine-grained material is found in the low-energy environments and gravels and sands in high-energy environments (Chester, 1990).

2.4 The chemical composition of average seawater and interstitial water

The gross chemical composition of seawater is not very geographically variable. Most of the 92 naturally occurring elements have been detected in seawater (Bearman, 1989a). Major seawater constituents (Table 2.1) are regarded as those which occur in concentrations greater than about 1 ppm.

The major constituents are responsible for more than 99.9 % of the salinity of seawater. According to Chester (1990), the salinity in surface ocean water ranges from ~32 to ~37 ‰, and Millero (1996) reports the total salinity of average seawater as being 35.2 ‰. The pH range in normal open-ocean seawater is ~7.5 to ~8.4 (Chester, 1990). On a geological time scale, this pH is controlled by chemical equilibria between the water and common minerals in the sediments. However, over a much larger time span (i.e. hundreds of thousands of years), equilibria between dissolved CO_2, bicarbonate ions, carbonate ions and hydrogen ions, regulate the pH of the oceans

(Chester, 1990). Wedepohl (1971) gives the pH of average seawater as 8.1±0.2.

Most of the major constituents in Table 2.1 exhibit conservative behaviour in seawater: their concentrations are not affected by the biological and chemical reactions that occur in the oceans. Only by the mixing of different water masses of varying salinity, can their concentrations be altered (Bearman, 1989a). However, the exceptions are calcium and carbon (bicarbonate, carbonate and dissolved organic carbon (DOC)). These major constituents are non-conservative.

The majority of the trace constituents in seawater (Table 2.2) behave non-conservatively. This is because they are both chemically and biologically reactive in the marine environment (Millero, 1996).

Table 2.1 Major constituents of average seawater (at salinity = 35 ‰).

Constituent	Concentration (mg/kg)
Chloride (Cl^-)	19837 (19834)
Sodium (Na^+)	11054 (11029)
Sulfate (SO_4^{2-})	2780 (2778)
Magnesium (Mg^{2+})	1316 (1322)
Calcium (Ca^{2+})	422 (422)
Potassium (K^+)	409 (409)
Bicarbonate (HCO_3^-)	110
Bromide (Br^-)	69 (69)
Boric acid ($B(OH)_3$)	19
Carbonate (CO_3^{2-})	16
Strontium (Sr^{2+})	8.1 (8.2)
Fluoride (F^-)	(1.3)
Borate ($B(OH)_4^-$)	1
Dissolved organic carbon (DOC)	(0.3-2.1)

Data sources for average seawater compositions are Millero (1996) and Drever (1997), the latter in parentheses.

Table 2.2 Concentrations of selected trace constituents in average seawater and probable main inorganic species in oxygenated seawater (at salinity = 35 ‰).

Element	Concentration (ppb)	Probable main inorganic species in oxygenated seawater
Aluminium	1 (0.4)	$Al(OH)_4^-$, $Al(OH)_3$
Manganese	0.2 (0.1)	Mn^{2+}, $MnCl^+$
Iron	2 (0.055)	$Fe(OH)_3$
Nickel	0.5 (0.48)	Ni^{2+}, $NiCO_3$, $NiCl^+$
Copper	0.5 (0.1)	$CuCO_3$, $CuOH^+$, Cu^{2+}
Zinc	2 (0.5)	Zn^{2+}, $ZnOH^+$, $ZnCO_3$, $ZnCl^+$
Cadmium	0.05 (0.1)	$CdCl_2$, $CdCl^+$, $CdCl_3^-$
Lead	0.03 (0.002)	$PbCO_3$, $Pb(CO_3)_2^{2-}$, $PbCl^+$

Data sources for average seawater concentrations are Drever (1997) and Bearman (1989b), the latter in parentheses. Species data obtained from Chester (1990).

Despite the relatively high concentrations of nitrogen and silicon in seawater (i.e. >1 mg/L) (Table 2.3), these components are not regarded as major constituents. This is because nitrogen and silicon (as well as phosphorus) are the major micronutrients for marine organisms. In addition, N is largely present as a dissolved gas. Hence, these three elements are non-conservative. Silicon in particular is strongly non-conservative.

Table 2.3 Concentrations of micronutrients in seawater

Nutrient	Total concentration (mg/L)
Nitrogen	11.5
Silicon	2
Phosphorus	0.06

Source of data is Bearman (1989a).

The interstitial water-sediment system is an area of high chemical, physical and biological activity. Consequently, new or altered mineral phases are often formed in the sediments and the composition of the pore waters can be changed significantly.

These changes are collectively termed diagenesis. Bearman (1989b) describes diagenesis as, the chemical changes that occur in sediments through interaction with pore waters, subsequent to the deposition of the material in water. Many of the chemical changes that take place during early diagenesis are redox-mediated. In turn, the redox state is controlled by the amount of organic carbon in the sediment system. Diagenesis proceeds by using oxidants in the order: oxygen > nitrate > manganese oxides > iron oxides > sulfate (Chester, 1990).

Interstitial waters differ from seawater with respect to some major components. The pore waters are usually enriched in Na^+, Ca^{2+} and HCO_3^-, and depleted in K^+ and Mg^{2+} relative to seawater (Chester, 1990). Changes in Ca^{2+} can result from the dissolution of $CaCO_3$ due to the production of CO_2 by the oxidation of plant matter. Mg^{2+} may be depleted due to uptake by chlorite or interactions with $CaCO_3$ to form dolomite (Millero, 1996). Changes in K^+ as well as other cations can occur by exchange with clay minerals. Chester (1990) explains that K^+ concentrations often decrease with sediment depth because of the formation of potassium feldspar. Millero (1996) claims however, that K^+ can be enriched in pore waters due to the hydrolysis of feldspars. The Cl^- level in interstitial waters is usually within ± 1 % of the overlying water (Millero, 1996).

The fate of trace metals in sediment pore waters is largely controlled by their mobility in the sediment. Elements that are concentrated in interstitial waters relative to seawater can either be released into the seawater or they can be re-incorporated into sediment components.

2.5 Types of metal interactions in sediments

Most of the biogeochemical activity in sediments occurs in the surface layer. It is this portion of the sediment that has the greatest effect on the quality of the overlying water. Within the sediment movement of solutes takes place by molecular diffusion (Van Cappellen and Wang, 1995).

Five main sources of natural metal accumulations in marine environments have been

identified (Förstner and Wittmann, 1979; Yen and Tang, 1977):

(a) *Lithogenous sediment* is material derived mainly from the weathering of silicate and carbonate rocks on the continents.
(b) *Biogenous sediment* contains decomposition products of organic substances as well as inorganic siliceous and calcareous shells.
(c) *Hydrogenous sediment* is material formed by chemical reactions in the water-sediment system, e.g. products of precipitation.
(d) *Atmogenous sediment* is material containing metals derived from atmospheric fall-out.
(e) *Cosmogenous sediment* is composed of extra-terrestrial particles.

The processes that are responsible for the association of trace metals with the solid phase in sediments include metal precipitation and coprecipitation, adsorption, complexation and the incorporation of metals into crystalline sediment components.

2.5.1 Precipitation of metals

The solubility product principle is applied to a saturated solution in which a dynamic equilibrium exists between a solid substance and its aquated ions, for example:

$$MX_{2(s)} \leftrightarrow M^{2+}{}_{(aq)} + 2X^{-}{}_{(aq)}$$

The solubility product (K_{sp}) can be described as:

$$K_{sp} \text{ for } MX_2 = [M^{2+}]\ [X^{-}]^2$$

During precipitation the concentration of a metal ion is primarily dependent on the type and activity of the anionic species in solution, as well as the pH of the solution. In surface water and pore water of sediments, the dominating ions include chloride, sulfate, bicarbonate and (under reducing conditions) anionic species derived from hydrogen sulfide. The chlorides (except silver and mercury chloride) and sulfates of all metals are readily soluble, whereas the carbonates, hydroxides and sulfides are fairly

insoluble (Förstner and Wittmann, 1979).

(i) *Oxyhydroxides*

Metal oxyhydroxides can precipitate in several forms, which may behave differently during coprecipitation or dissolution reactions. Generally, the most chemically active form is the amorphous or very fine crystalline precipitate, which forms in highly oversaturated solutions. These precipitates may remain in metastable equilibrium with the solution and may slowly convert to a more stable and less active form. For example, $Fe(OH)_3$ and FeOOH may age to the more stable Fe(III) phase, hematite (Fe_2O_3). The inactive solid phases may also form from solutions that are only slightly oversaturated (Förstner and Wittmann, 1979).

(ii) *Sulfides*

Heavy metal sulfides are almost completely insoluble at neutral pH. The sulfides of Fe, Mn and Cd are readily soluble in hydrochloric acid, whereas other metal sulfides, such as those of Cu and Pb, are only soluble in oxidising acids, for example nitric acid (Förstner and Wittmann, 1979).

(iii) *Carbonates*

The solubility of carbonates in aqueous solution is dependent on the partial pressure of CO_2. For example, the solubility of $PbCO_3$ in distilled water (about 2.1 mg/L) can be increased by a factor of seven in the presence of CO_2, since dissolution is facilitated by the formation of bicarbonate:

$$PbCO_3 + H_2O + CO_2 \leftrightarrow Pb^{2+}_{(aq)} + 2(HCO_3)^-_{(aq)}$$

As a result, all carbonates are more soluble in the presence of CO_2 (Drever, 1997).

Oxyhydroxides, sulfides and carbonates will precipitate when the respective solubility products have been exceeded. (Drever, 1997).

2.5.2 Cation exchange and adsorption

Many of the sediment forming materials with large surface areas, particularly clay minerals, amorphous iron oxyhydroxides, amorphous silicic acids and organic substances, are involved in sorbing cations from solution and releasing equivalent amounts of other cations. This is called cation exchange and it is largely based on the sorptive properties of negatively charged anionic sites, such as SiOH-, $AlOH_2$- and AlOH-groups in clay minerals, FeOH-groups in iron oxyhydroxides, and carboxyl and phenolic OH-groups in organic substances (McBride, 1994).

Cation exchange is an example of electrostatic adsorption, where ions in solution are attracted by a surface of the opposite electrical charge. Other adsorption mechanisms include physical adsorption, where the attraction to the solid surface is due to relatively weak van der Waals forces, and chemical adsorption, where there is chemical bonding between the solute molecule and one or more atoms on the surface of the solid (Drever, 1997).

The sum of exchangeable cations is termed the "exchange capacity" and is expressed in cmoles/kg material (McBride, 1994). The exchange capacities of the common clay minerals increase in the order, kaolinite < chlorite < illite < montmorillonite, the latter having the smallest particle size and largest surface area. The exchange capacity of organic material is especially high, particularly that of humic acids.

2.5.3 Sorption onto clay minerals

pH is the main factor controlling the processes of heavy metal adsorption onto clay minerals, since the H^+ ions compete with the metal cations for exchange sites. Under acidic conditions, complete removal of metal cations from exchange sites can occur. The following sequence for the affinity of heavy metals toward clay minerals has been observed: Pb > Ni > Cu > Zn (Förstner and Wittmann, 1979). Although this trend is not fully understood, the valence of the ions, their hydration behaviour, electron negativity and ionisation potential are known to play important roles.

Clays have been described by Luther (1995) as the most common minerals which contain trace metals, however, they are typically resistant to attack by microbes and chemicals (including strong acids). Hence, they are regarded to be less important than Fe and Mn oxyhydroxides or Fe sulfides, in trace metal cycling. It has been suggested that the dominant role of clay minerals in the adsorption of metal cations is that of a mechanical substrate for the precipitation and flocculation of organics and secondary minerals (Sposito, 1989; Schlautman and Morgan, 1994).

2.5.4 Sorption and coprecipitation on Fe, Mn and Al oxyhydroxides

Iron, manganese and aluminium oxyhydroxides are examples of secondary minerals that demonstrate high adsorption affinities for heavy metals. The processes involved are adsorption and co-precipitation.

The oxyhydroxides of aluminium, iron and manganese, especially the redox-sensitive Fe- and Mn hydrous oxides under oxidising conditions, act as effective sinks for heavy metals in marine sediments (Förstner and Wittman, 1979; Honeyman and Santschi, 1992; Drever, 1997). Oxyhydroxides of Fe and Mn occur as coatings on clay minerals and as discrete grains of oxide mineral. The hydrous iron oxide usually occurs in an amorphous form, although the aged-crystallised form can be found in ancient sedimentary rocks. Crystallisation of the Fe and Mn oxyhydroxides reduces the surface area of the solid phases and it may alter the types of hydroxyl groups situated on the surface (Luoma and Davis, 1983). Manganese is frequently present as poorly crystallised birnessite (δ-MnO_2). The composition of this mineral ranges from $MnO_{1.6}$ to $MnO_{1.95}$. Other cations besides Mn may be present in birnessite (Drever, 1997). Hydrous oxides of Fe and Mn are extremely fine grained and typically have surface areas of 200 m^2/g. Aluminium is also associated with fine grained material and Al content is often a good indicator of the amount of fine grained material present in a sediment sample (Regnier and Wollast, 1993).

The iron compounds most commonly involved in reactions at the solid-solution interface are amorphous $Fe(OH)_3$ (ferrihydrite), Fe_3O_4 (magnetite), amorphous FeOOH and α-FeOOH (goethite). The scavenging capacity of Mn oxides for heavy metals is

greater than that of Fe and this is attributed to the very complex mineral structure of these oxides. Manganese exists in several oxidation states, it forms non-stoichiometric oxides with variable valency states and its higher oxides exist in several crystalline or amorphous forms (Hall *et al.* 1996). Usually, MnOOH species contain mixtures of Mn(II) and (IV) or Mn(III) (Förstner and Wittmann, 1979).

The negative surface charges of Fe and Mn oxyhydroxides increase with increasing pH and at high pH metal cations are strongly adsorbed. Metals bind to the hydrous oxides by interacting with the surface hydroxyl groups. Metals can also bind to MnO_2 by exchange of the metal cation for Mn(II) or by oxidation of the trace metal by Mn(IV) (Luoma and Davis, 1983). It is suggested that the mechanisms involved in the interactions between hydrous manganese oxides and trace metals involve adsorption as well as phase transformations in the Mn-oxyhydroxides and catalysis of redox reactions by the Mn^{2+} - Mn oxide system.

$$\text{-Mn-OH}^0 + M^{2+} \rightarrow \text{-Mn-OM}^+ + H^+ \text{ (Drever, 1997).}$$

In sediments where trace metal concentrations are controlled by adsorption on Fe and Mn hydrous oxides, the metal mobilities can be expected to be influenced by pH and Eh. Eh-pH diagrams are a convenient way of displaying stability relationships that involve redox reactions. Figures 2.1 and 2.2 show Eh-pH diagrams for the systems Fe-C-O-H and Mn-O-H respectively. These diagrams represent equilibrium relationships, but it is important to remember that natural systems are frequently in a state of non-redox-equilibrium. The limitation of equilibrium calculations is that they provide an indication of what reactions should occur but they fail to reveal at what rate they should take place (Drever, 1997). It should also be noted, that the Eh-pH diagrams presented in this chapter are simplified representations of real systems and do not take important seawater constituents such as chloride into account.

In Figure 2.1, $Fe(OH)_3$ is assumed to be the stable Fe(III) phase. The system is characterised by a large field of $Fe(OH)_3$, a large field of Fe^{2+}, and under reducing, basic conditions, a field of $Fe(OH)_2$. A small field of $FeCO_3$ (siderite) exists in the pH range 6.8 to 9.4, separating Fe^{2+} from $Fe(OH)_2$. Fe_3O_4 (magnetite) is not considered in

this diagram, and both Si and S are excluded from the system.

Mn^{2+} occupies most of the field in Figure 2.2, and the oxides and oxyhydroxides of Mn can exist only under basic pH except at high Eh. Various MnO_2 polymorphs (e.g. pyrolusite and todorokite) are likely to be present in an alkaline environment at moderate Eh.

Iron(II) readily oxidises at lower pH than manganese(II). Inorganic Fe(II) oxidises at pH values of >5 whereas inorganic Mn(II) only oxidises at pH values of >8.5 (Luther, 1995). If a negative redox potential causes the metal oxides to dissolve, the adsorbed metals will be released.

They may enter the aqueous phase or be precipitated by some other phase such as metal sulfides. As soon as an oxic environment is maintained, precipitation of Fe and Mn will occur (Regnier and Wollast, 1993). Ferrous iron is stable in the presence of dissolved oxygen under acidic conditions, and ferric iron exists at high Eh and at very acidic pH. If the conditions become reducing, $Fe(OH)_3$ can be converted into $FeCO_3$ in the presence of CO_2. At even lower oxygen levels, iron sulfide minerals will form.

2.5.5 Sorption and coprecipitation on Fe and Mn sulfides

It has long been accepted that sulfide minerals play an important role in controlling trace metal chemistry in anoxic marine sediments (Förstner and Wittmann, 1979; Stumm, 1992; Luther, 1995; Morse, 1995; Cooper and Morse, 1998a). Sulfide phases are formed in anoxic and sulphidic environments when sulfide attacks and dissolves the oxide and hydroxide phases. This process reduces Fe(III) to Fe(II), resulting in the precipitation of FeS and FeS_2.

Figures 2.3 and 2.4 show Eh-pH diagrams for the systems Fe-S-O-H and Mn-C-S-O-H respectively. In Figure 2.3, hematite (Fe_2O_3) is shown as the stable Fe(III) phase. Both $Fe(OH)_3$ and FeOOH (represented in Figure 2.1) may age slowly to Fe_2O_3. A large field of FeS_2 (pyrite) exists below the sulfide-sulfate boundary. Fe_3O_4 (magnetite) may appear above a pH of about 9 and in a reducing environment. Under strongly

reducing conditions and at highest pH, a very small FeS (pyrrhotite) field may arise.

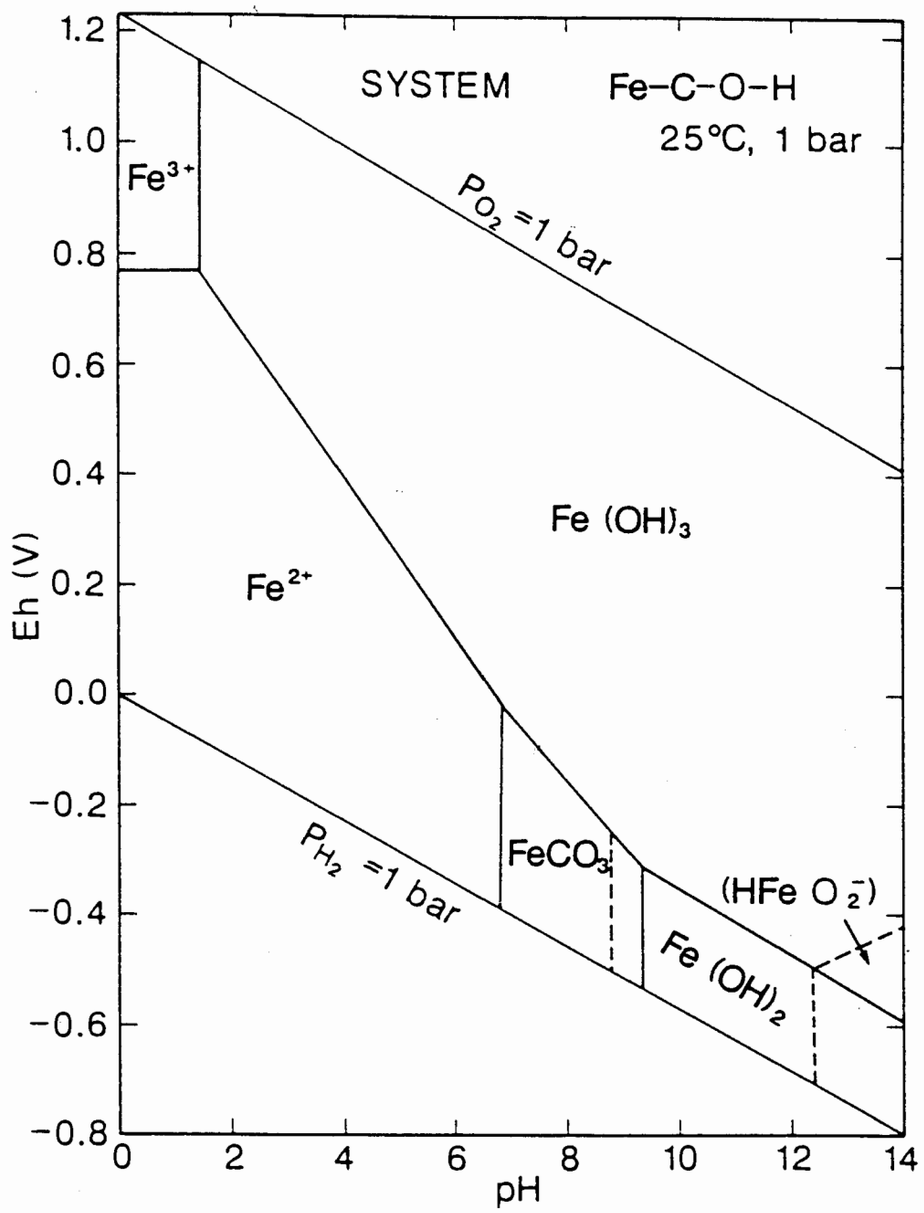


Figure 2.1 Eh-pH diagram for part of the system Fe-C-O-H.
Assumed activities for dissolved species are: Fe = 10^{-6}, C = 10^{-3} (After Brookins, 1988).

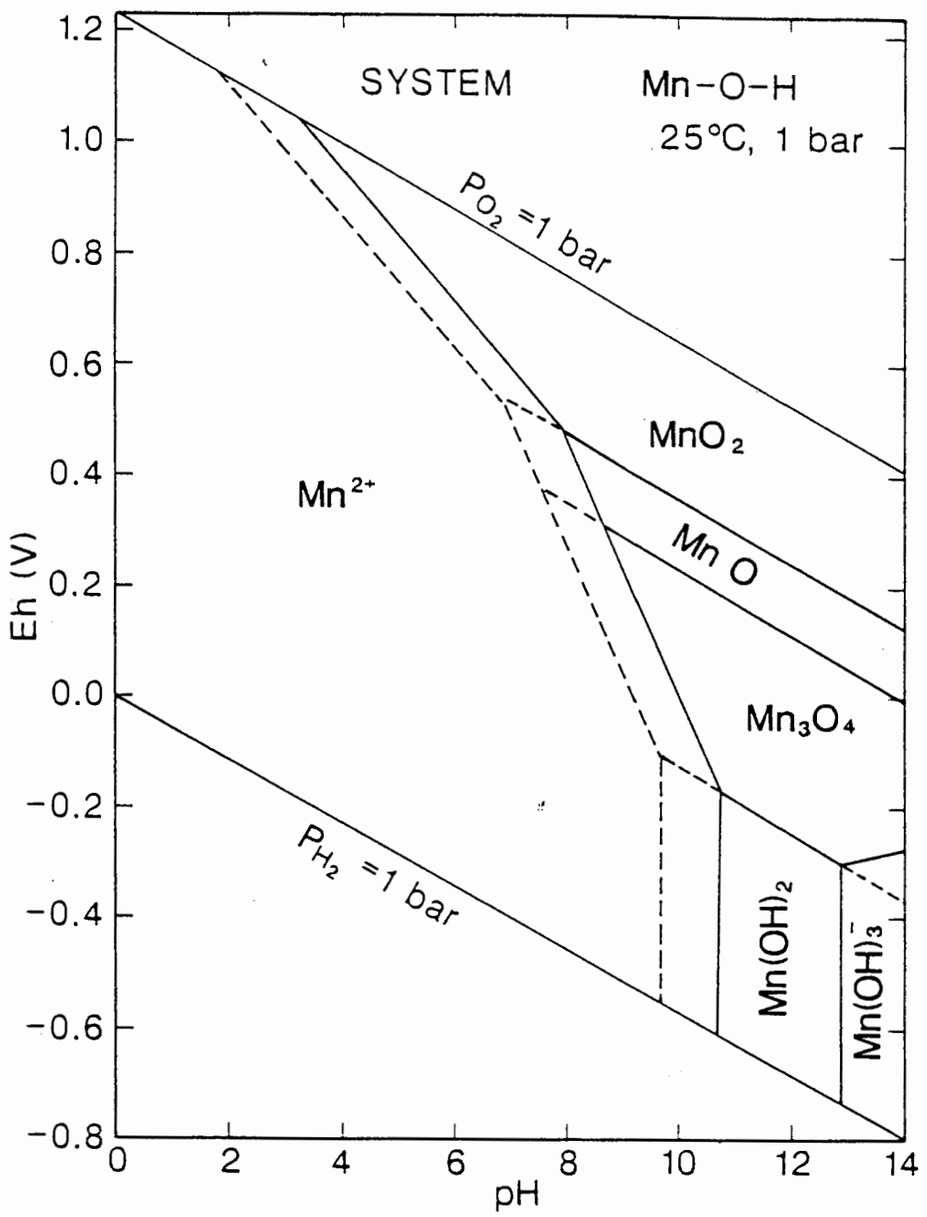


Figure 2.2 Eh-pH diagram for part of the system Mn-O-H. Assumed activity for Mn = 10^{-6} (After Brookins, 1988).

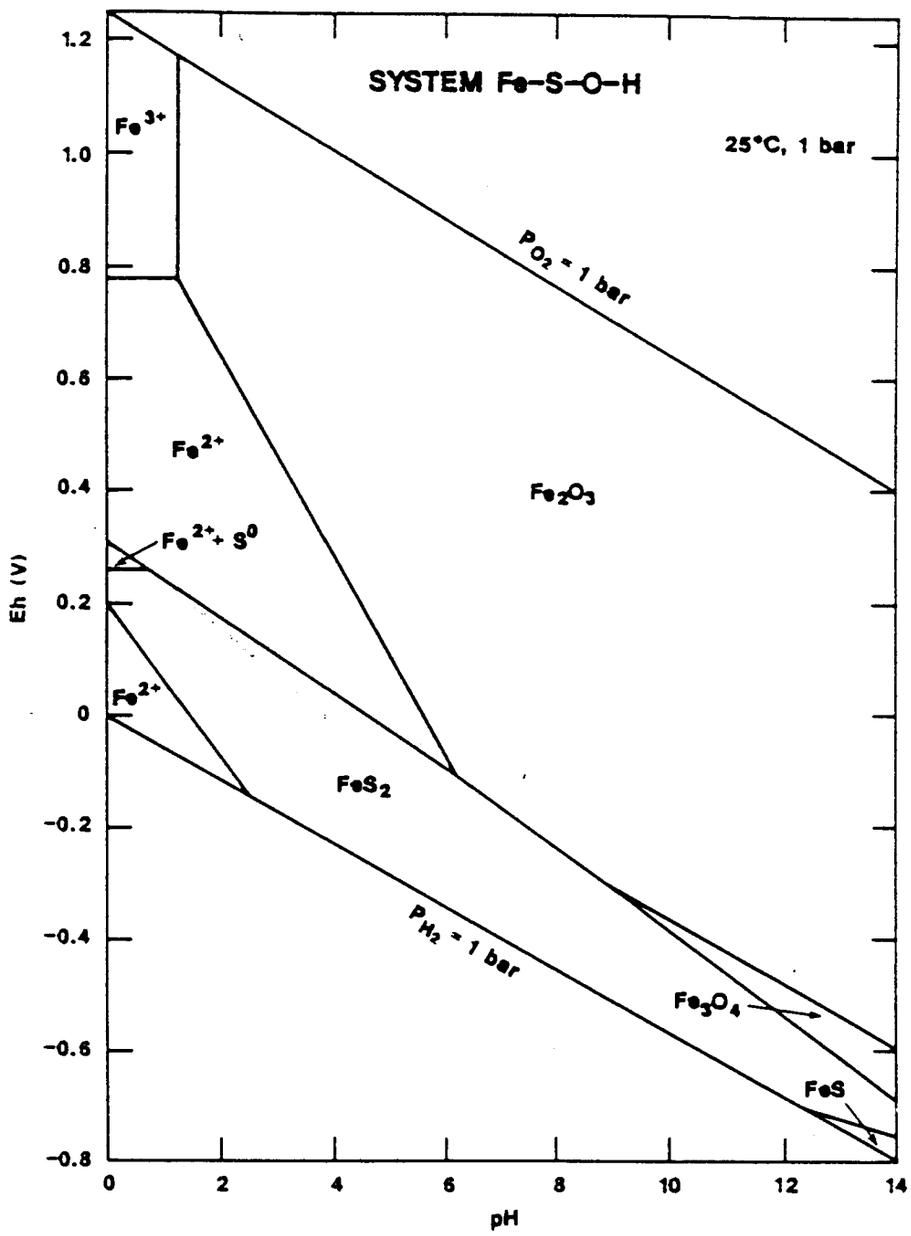


Figure 2.3 Eh-pH diagram for part of the system Fe-S-O-H. Assumed activities of the dissolved species are: Fe = 10^{-6}, S = 10^{-3} (After Brookins, 1988).

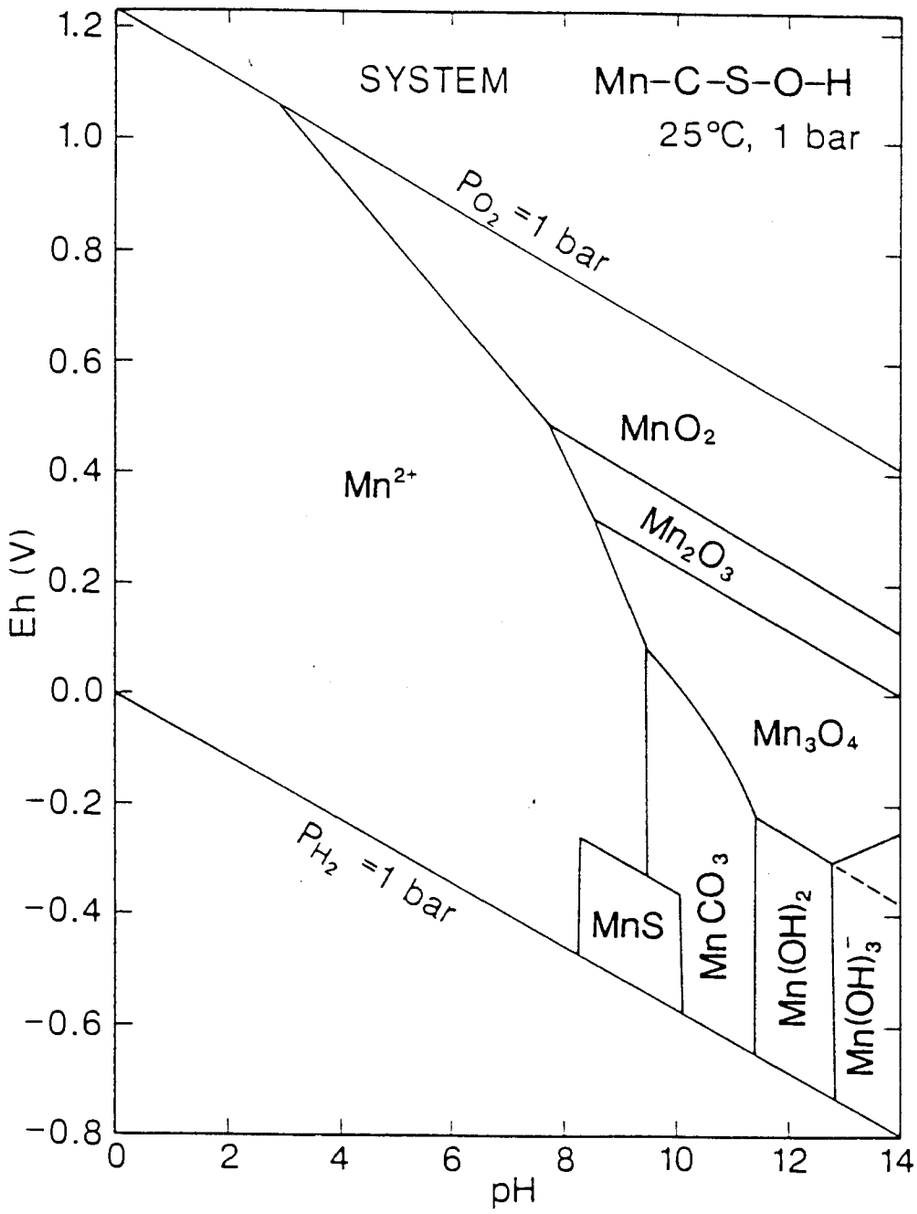


Figure 2.4 Eh-pH diagram for part of the system Mn-C-S-O-H. Assumed activities of the dissolved species are: Mn = 10^{-6}, C = 10^{-3}, S = 10^{-3} (After Brookins, 1988).

Figure 2.4 shows the effect of adding carbon and sulfur to the Mn-O-H system (shown in Figure 2.2). The field of MnCO3 (rhodochrosite) is significant, as it can exist just above the sulfide-sulfate boundary, or Mn in $MnCO_3$ can be fixed with cogenetic sulfides (Brookins, 1988). A small field of MnS (alabandite) may appear in reducing and alkaline conditions. However, this mineral is very rare in nature (Brookins, 1988).

Sediments in which sulfate is reduced to sulfide at the sediment-water interface, typically contain a large percentage of silt and clay-sized material, more than 0.5 wt% organic carbon, and accumulate at moderate to high sedimentation rates (Morse, 1995).

Bacteria oxidise the organic matter via the reduction of sulfate and produce sulfide:

$$\text{organic matter} + SO_4^{2-} - \text{bacteria} \rightarrow H_2S$$

The H_2S interacts with sedimentary iron minerals to form metastable iron sulfide minerals, which include amorphous FeS, mackinawite (FeS), and greigite (Fe_3S_4).

These minerals are operationally defined as acid volatile sulphides (AVS), as they dissolve and produce H_2S when reacted with hydrochloric acid (Cooper and Morse, 1998a).

$$\text{reactive-Fe} + H_2S \rightarrow \text{AVS}$$

Compared to pyrite, greigite and mackinawite are thermodynamically unstable, and are usually transformed to pyrite during early diagenesis:

$$FeS_{\text{mackinawite}} + S \rightarrow FeS_{2\ \text{pyrite}}$$

$$Fe_3S_{4\ \text{greigite}} + 2\,S \rightarrow 3\,FeS_{2\ \text{pyrite}}$$

The oxidation of metal sulfides can play a significant role in the mobilisation of trace metals associated with the solid phase (Förstner and Wittmann, 1979; Regnier and

Wollast, 1993; de Groot, 1995; Luther, 1995; Pardue and Patrick, 1995).

2.5.6 Associations with organic substances

Trace metals generally interact strongly with organic matter, and this is usually via chelation (Drever, 1997). The complexation of trace metals by dissolved organic matter can greatly increase the concentration of the metals in solution. This effect is more important in interstitial water than in overlying waters, as pore water organic matter concentrations are typically 10-50 times greater than those of the overlying waters (Bufflap *et al.*, 1995).

Adsorption onto solid organic matter can result in metals being removed from solution. The detailed mechanisms of metal adsorption by organic matter are still unknown (Drever, 1997). However, increased adsorption at high pH has been shown to involve phenolic hydroxyl groups. The NH_2 groups in amino acids also act as significant binding sites for trace metals, particularly for Cu (Buffle, 1988). Weak attractive forces between metal cations and organic matter are usually associated with physical adsorption, whereas strong attractive forces are attributed to chemical bonds, as in chelation. In deep-sea environments, trace metals show greatest affinity for Fe and Mn oxyhydroxides. In nearshore sediments, however, these sorption phases are in competition with organic matter for metal cations, as coastal sediments typically have a higher organic matter content. The overall importance of organic matter and Fe and Mn oxyhydroxides as metal scavengers is related to their abundance in the sediment (Cundy and Croudace, 1995). If solid surfaces such as clay minerals are covered with organic material, they may demonstrate the chemical properties of the organic matter (Schlautman and Morgan, 1994).

Humic substances are the most important products formed by the decomposition of organic material. They are extremely heterogeneous polymers and are characterised by their variable molecular mass. According to Schlautman and Morgan (1994), humic substances represent the largest fraction of the organic carbon (40-60 %) present in natural water systems. Humic substances are operationally separated into humic acid, fulvic acid and humin according to their solubility in strong acid and base. Aqueous

sodium hydroxide extracts humic and fulvic acid from sediments, leaving the humin behind (McBride, 1994). Humic acids belong to the middle molecular size range, are very complex and are soluble in natural systems under certain conditions. Fulvic acids are described by Förstner and Wittmann (1979) as being less condensed humic substances which play a highly significant role in the bonding of metals because of their large number of functional groups. They usually occur in a dissolved state.

The Irving-Williams stability series has been used to establish the order of organometallic-complex stability. The series states that for almost every ligand the stability of its complexes increases in the order (Millero, 1996):

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

In laboratory work conducted by Wells *et al.* (1998), the addition of Cu to seawater samples did not displace Zn from the organic complexes, even though theoretically (according to the Irving-Williams stability series), Cu should form much more stable organic complexes than Zn. Wells *et al.* (1998) suggested that this may be attributed to the ability of biological systems to produce highly metal-specific organic molecules. The lack of Zn displacement by Cu may also be attributed to the fact that both metals have an affinity for sulfur-containing binding sites (Drever, 1997).

2.5.7 Sorption of trace metals on carbonates

Although the trace metal content of carbonates is relatively low, the surface energy of the substances is sufficiently high to allow for adsorption processes to occur. It is suggested that the extent of metal adsorption on carbonate surfaces is similar to that of some clay minerals, such as kaolinite. Luoma and Davis (1983) suggest that the low specific surface areas of carbonates greatly reduce their metal binding capacities. It is likely that co-precipitation with carbonate minerals may be an important mechanism for some metals, such as zinc and cadmium (Förstner and Wittmann).

The precipitation of calcium carbonate is inhibited by dissolved organic matter (Förstner and Wittmann, 1979) and dissolved Mg plays an important role in the

inhibition of calcite and dolomite in seawater (Berner, 1975; Morse, 1986). Most of the Mg inhibition is due to the incorporation of Mg into growing calcite and dolomite crystals, causing them to become more soluble. Mg ions also inhibit the low temperature transformation of aragonite to calcite (Berner, 1975). Together with the sorption processes that occur on hydrous oxides of Fe, Mn and Al, the co-precipitation of trace metals with calcium carbonate plays a significant role in the removal of trace metals from solution.

2.6 Cadmium, copper, lead and zinc in sediments

Cd, Cu, Pb and Zn demonstrate similar behaviour in aquatic systems. The divalent cation is the dominant species in solution. Under oxidising conditions, their solubilities at high pH values are greatly affected by the solubilities of the relevant carbonates and oxyhydroxides (Figures 2.5 to 2.8). Under reducing conditions and in the presence of sulfur, all four trace metals form insoluble metal sulfides. When sulfur is absent, Cu is present as insoluble Cu metal, whereas Cd, Zn and Pb behave as they do in oxidising environments: they are fairly soluble at low pH and form insoluble carbonates and oxides at higher pH values. Changes in redox conditions affect the metals by controlling the solubilities of the redox reactive adsorption phases: sulfides and Fe/Mn oxyhydroxides. Cu, Cd, Zn and Pb are all complexed by organic matter, copper being complexed to the greatest extent.

2.6.1 Cadmium in sediments

(a) *Chemistry and geochemistry of cadmium*

Cadmium is a relatively rare element in the lithosphere: its abundance is ranked 67th. The average concentration of Cd in the earth's crust is about 0.1 mg/kg. Sedimentary rocks show the greatest range of Cd concentrations than any other rock type, with phosphorites (sedimentary Ca phosphates) and marine black shales typically containing the greatest concentrations (<10-980 mg/kg and 0.30-219 mg/kg respectively) (Alloway, 1995b). Geochemically, Cd is associated with Zn, as both elements have similar ionic structures and electronegativities and both are highly

chalcophilic (although Cd possesses a stronger affinity for S than does Zn). Common hosts for Cd include the ZnS minerals sphalerite and wurtzite, as well as smithsonite ($ZnCO_3$). Levels of Cd in these minerals range from 0.2 % to 5 %. Sediments and soils typically contain less than 1 mg Cd/kg, unless they are derived from parent material containing unusually high concentrations of Cd (such as black shale), or the soil is contaminated (McBride, 1994; Alloway, 1995b).

(b) *Behaviour of cadmium in sediments*

Cadmium is a second row transition element. The dominant species of Cd in sediment and soil solutions is Cd^{2+} but Cd can form a range of species including, $CdCl^+$, $CdOH^+$, $CdHCO_3^+$, $CdCl_3^-$, $CdCl_4^{2-}$, $Cd(OH)_3^-$ and $Cd(OH)_4^{2-}$ as well as organic complexes. The concentrations and speciation of Cd in solution depend on the levels of the ligands in solution as well as the stability constants of the metal-ligand complexes. Various aspects of Cd chemistry can be explained by the hard-soft Lewis acid-base principle (HSAB). Cd is a soft Lewis acid and will react to form complexes with soft Lewis bases, such as S^{2-} (Shriver *et al.* 1990). Although hydroxyl groups and chloride ligands are classified as hard bases and borderline bases respectively (Shriver *et al.*, 1990), Cd forms a variety of soluble complexes with these groups. The stable complexation of Cd with chloride ions is well known (Regnier and Wollast, 1993; Alloway, 1995b; Sung, 1995; Comber *et al.*, 1995; Sirinawin *et al.*, 1998). In surface seawaters, Cd associates weakly with suspended particulate matter and is present mainly in solution in the form of Cd-chloro complexes (Comber *et al.*, 1995; Sirinawin *et al.* 1998). In oxic sediments however, humic substances (Fu *et al.*, 1992) as well as iron oxide (Oakley *et al.*, 1981) have been reported to be the major adsorbing phases for Cd. Organic matter appears to be the most important factor involved in Cd^{2+} sorption by soils (Lee *et al.*, 1996).

Below the sulfide-sulfate boundary in Figure 2.5, a large field of CdS (greenockite) exists, although in nature a large proportion of the Cd under these conditions may be obscured by Zn in minerals such as sphalerite. Above this boundary, a large field is occupied by Cd^{2+} under slightly basic to very acidic pH. As conditions become more alkaline, $CdCO_3$ forms, then $Cd(OH)_2$, followed by aqueous CdO_2^{2-}. Above a pH of

about 8, Cd may also co-precipitate with $CaCO_3$. Concentrations of Cd in solution are known to decrease with an increase in pH, due to increases in hydrolysis and negative charges on adsorption phases (Alloway, 1995). Below a pH of about 6, Cd^{2+} tends to adsorb weakly on organic matter, clay minerals and oxides.

(c) *Sources of cadmium contamination*

Sources of contamination in natural systems include the mining and smelting of Pb and Zn; air-borne pollution from metallurgical industries, the incineration of Cd-containing wastes such as plastics and batteries, sewage sludges; and fossil fuel burning (Alloway, 1995).

2.6.2 Copper in sediments

(a). *Chemistry and geochemistry of copper*

Like all elements in the first transition series, the removal of two electrons from copper atoms can be achieved quite easily. The concentration range of Cu in the earth's crust is 24-55 mg/kg and it is ranked 26th in the order of elemental abundance in the lithosphere. (Baker and Senft, 1995). Chalcopyrite ($CuFeS_2$) is the most abundant copper mineral. The Cu content of basaltic rocks (30-160 mg/kg) is greater than that of granitic rocks (4-30 mg/kg), and Cu concentrations in carbonate rocks are very low (5-20 mg/kg). Black shales (20-200 mg/kg) and basalt rocks (30-160 mg/kg) have the highest Cu concentrations (Baker and Senft, 1995).

(b) *Behaviour of copper in sediments*

Copper in sediments is usually present as Cu^{2+}, but the conversion of Cu^{2+} (cupric) to Cu^{+} (cuprous) and eventually to Cu^{0} (native copper) can occur under reducing conditions, particularly if soft Lewis bases such as sulfide ions are present to stabilise Cu^{+}, which is a soft Lewis acid. In addition, the second ionisation energy of copper is substantially higher than the first, which allows for a variety of Cu(I) species to exist in nature (Baker and Senft, 1995).

The Eh-pH diagram for part of the system Cu-C-S-O-H (Figure 2.6) shows a fairly large field of Cu^{2+} exists under oxidising and acidic conditions.

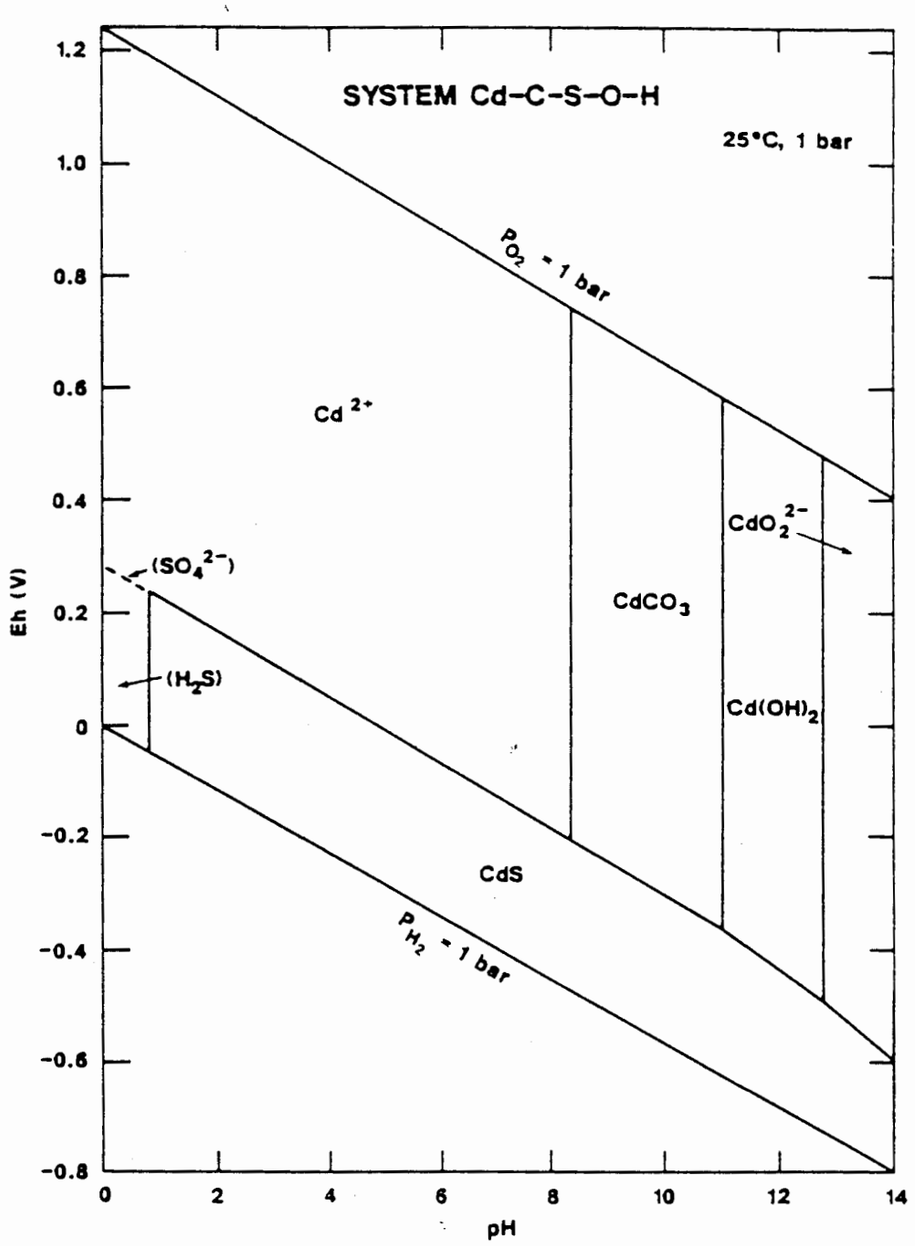


Figure 2.5 Eh-pH diagram for part of the system Cd-C-S-O-H. The assumed activities for the dissolved species are : Cd = 10^{-8}, C = 10^{-3}, and S = 10^{-3} (After Brookins, 1988).

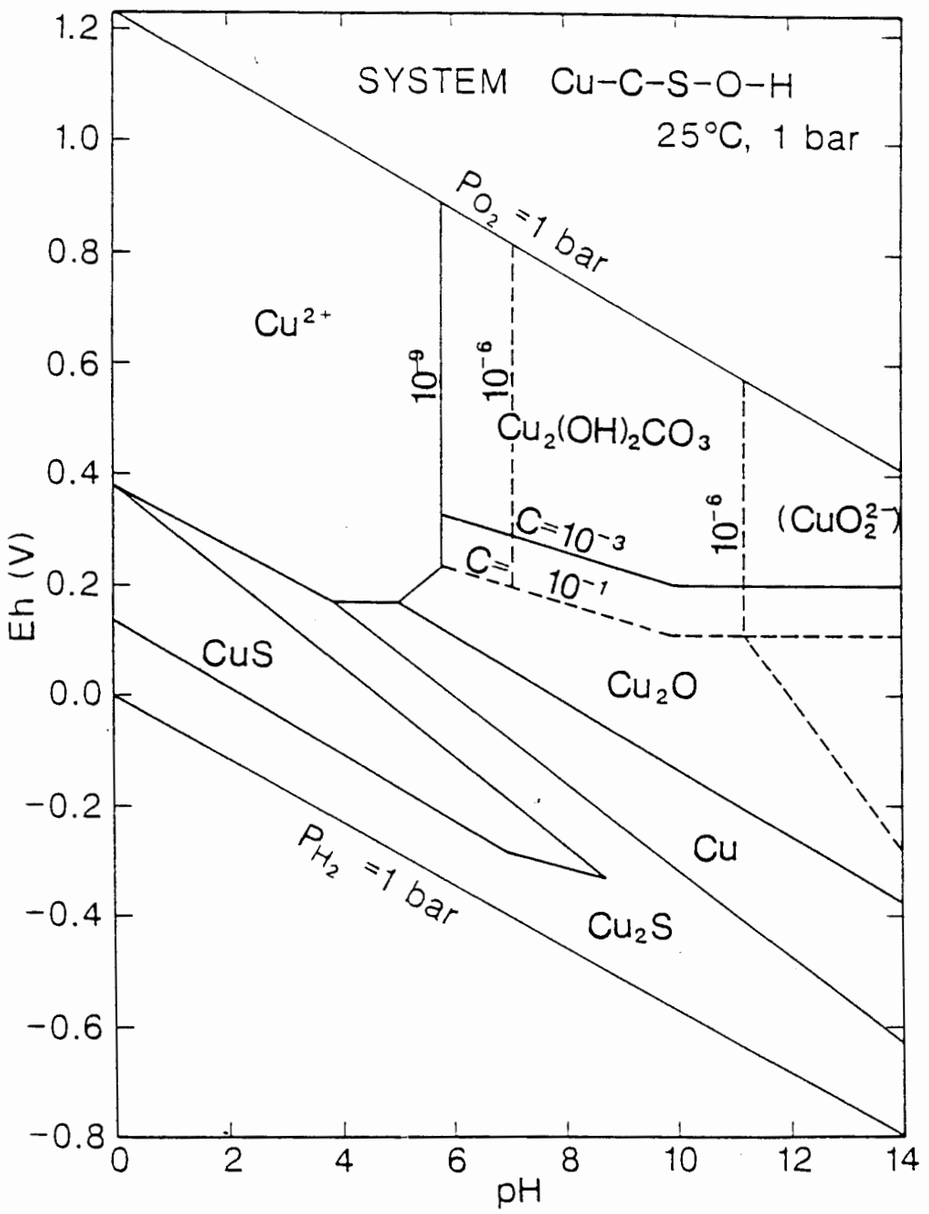


Figure 2.6 Eh-pH diagram for part of the system Cu-C-S-O-H. The assumed activities for the dissolved species are: Cu = 10^{-6}, S = 10^{-3}, C = $10^{-1,-3}$ (After Brookins, 1988).

Malachite ($Cu_2(OH)_2CO_3$) is the most important Cu(III) carbonate in this system, as azurite is a metastable polymorph. Precipitation of malachite and azurite as well as cupric hydroxide or cupric oxide, are possible in sediments with relatively high Cu levels at a pH greater than 6.

Copper is a chalcophile and in reduced environments forms insoluble sulfide minerals. Two important sulfides occur below the sulfide-sulfate boundary : Cu_2S (chalcocite) and CuS (covellite) both occupy significant sections of the Eh-pH diagram. Figure 2.6 indicates that as sulfide becomes sulfate above the sulfide-sulfate boundary, Cu^+ from chalcocite is reduced to native Cu.

Although the solubility of free Cu^{2+} in alkaline environments is very low, soluble complexes of Cu^{2+} (in particular, hydroxy, carbonate and organic matter complexes) form and increase the total copper solubility. This allows for significantly higher Cu solubility under high pH conditions.

Most of the copper in sediments and surface soils, especially at higher pH, tends to be in the form of Cu^{2+}-organic complexes (McBride, 1994; Comber *et al.*, 1995). Organically bound Cu is complexed more strongly than any other divalent transition metal (McBride, 1994). This is especially so when low levels of Cu are present in humic substances which contain highly selective functional groups, such as amines and polyphenols. However, according to Luoma (1986), Cu in estuarine sediments is not associated with one component exclusively, but that Cu distribution changes from sediment to sediment, depending on the different proportions of sediment components. Organic matter and oxides of iron and manganese (as opposed to the acid volatile sulfides) may be the principle binding phases responsible for removing Cu from pore water (Bufflap *et al.*, 1995). In seawater, complexation by organic matter is particularly important for Cu (Clegg and Sarmiento, 1989; Regnier and Wollast, 1993).

(c) *Sources of copper contamination*

High concentrations of copper in natural systems have been attributed to contamination from smelters, fertilisers, sewage sludges and other wastes, pesticides,

or livestock manures.

2.6.3 Lead in sediments

(a) *Chemistry and geochemistry of lead*

Lead can exist in two stable oxidation states, Pb(II) and Pb(IV). In sediments and soils it exists mainly as the plumbous ion, Pb^{2+}. The ionic radius of Pb^{2+} is 124 pm and it can replace K^{+} (133 pm) in silicate lattices or Ca^{2+} (106 pm) in carbonates and apatites by isomorphous substitution (Davies, 1995). Lead is also chalcophilic and is, therefore, often concentrated in sulfur-containing rocks.

The most abundant lead mineral is galena (PbS). In rocks, there is a tendency for lead concentrations to increase with increasing silica content: the average Pb concentration in gabbro is 1.9 mg/kg, in andesite it is 8.3 mg/kg, and in granite the average Pb content is 22.7 mg/kg (Davies, 1995). Sedimentary rocks, such as shales and mudstones, have an average Pb concentration of 23 mg/kg. Sandstones contain an average of 10 mg Pb/kg, while limestones and dolomites contain about 71 mg Pb/kg (Davies, 1995).

(b) *Behaviour of lead in sediments*

In reducing environments, the formation of very insoluble PbS occurs. Lead is the least mobile heavy metal in reducing environments (McBride, 1994). The Pb^{2+} cation is complexed very strongly by sulphhydryl groups found in humic substances. Under oxic conditions, Pb solubility decreases as the pH increases. This is due to the precipitation of Pb carbonate, hydroxide and phosphate at high pH, as well as complexing with organic matter and chemisorption on oxides and silicate clays (McBride, 1994; Davies, 1995). The solubility of Pb can increase in alkaline environments as soluble Pb-organic and Pb-hydroxy complexes are formed. The Pb^{2+} cation has a high affinity for Mn oxides, and this may be explained by the Mn oxidation of Pb^{2+} to Pb^{4+}, which is a very insoluble ion (McBride, 1994). Owing to the strong complexation of Pb by organic matter, Pb often bioaccumulates in the organic rich layers of sediments and soils.

Under reducing conditions, the Eh-pH diagram for part of the system Pb-S-C-O-H (Figure 2.7) is largely characterised by PbS. Native lead is metastable, as it falls below the lower stability limit of water in the presence of sulfur. Above the sulfide-sulfate boundary, S^{2-} is oxidised to S^{6+} but Pb^{2+} remains unchanged. Consequently, a very small field of Pb^{2+} exists at pH below 0.4. As the pH increases, a larger field of $PbSO_4$ (anglesite) arises, followed by $PbCO_3$ (cerussite), and then PbO (massicot or litharge). Under very oxidising conditions and neutral to basic pH, Pb^{2+} oxidises to Pb^{3+} (to form Pb_3O_4; minium) and Pb^{4+} (to form PbO_2; plattnerite). The field of Pb^{2+} is much larger at low concentrations of dissolved C and S (Brookins, 1988).

(c) *Sources of lead contamination*

According to Davies (1995), lead contamination in soils is widespread, except in remote areas that have not been impacted on by human settlements. Several well-known sources of lead contamination exist. They include mining and smelting activities, manures, sewage sludge and contamination from vehicle exhausts. The residence time of lead in soils is so long that lead contamination of soils is often regarded as permanent.

2.6.4 Zinc in sediments

(a) *Chemistry and geochemistry of zinc*

As a chalcophile, zinc tends to occur in rocks as the mineral sphalerite (ZnS). Other zinc sulfide minerals include, wurtzite (ZnS polymorph), smithsonite ($ZnCO_3$), willemite (Zn_2SiO_4), zincite (ZnO), zinkosite ($ZnSO_4$), franklinite ($ZnFe_2O_4$) and hopeite ($Zn_3(PO_4)_2.4H_2O$). Average Zn concentrations vary from 40 mg/kg in granites to 100 mg/kg in basaltic rocks. In sedimentary rocks, the highest Zn levels are found in shales and clayey sediments (80-120 mg/kg), whereas sandstones, limestones and dolomites typically have lower Zn concentrations (10-30 mg/kg). The common range for total zinc in soils is 10-300 mg/kg (average content of 50 mg/kg).

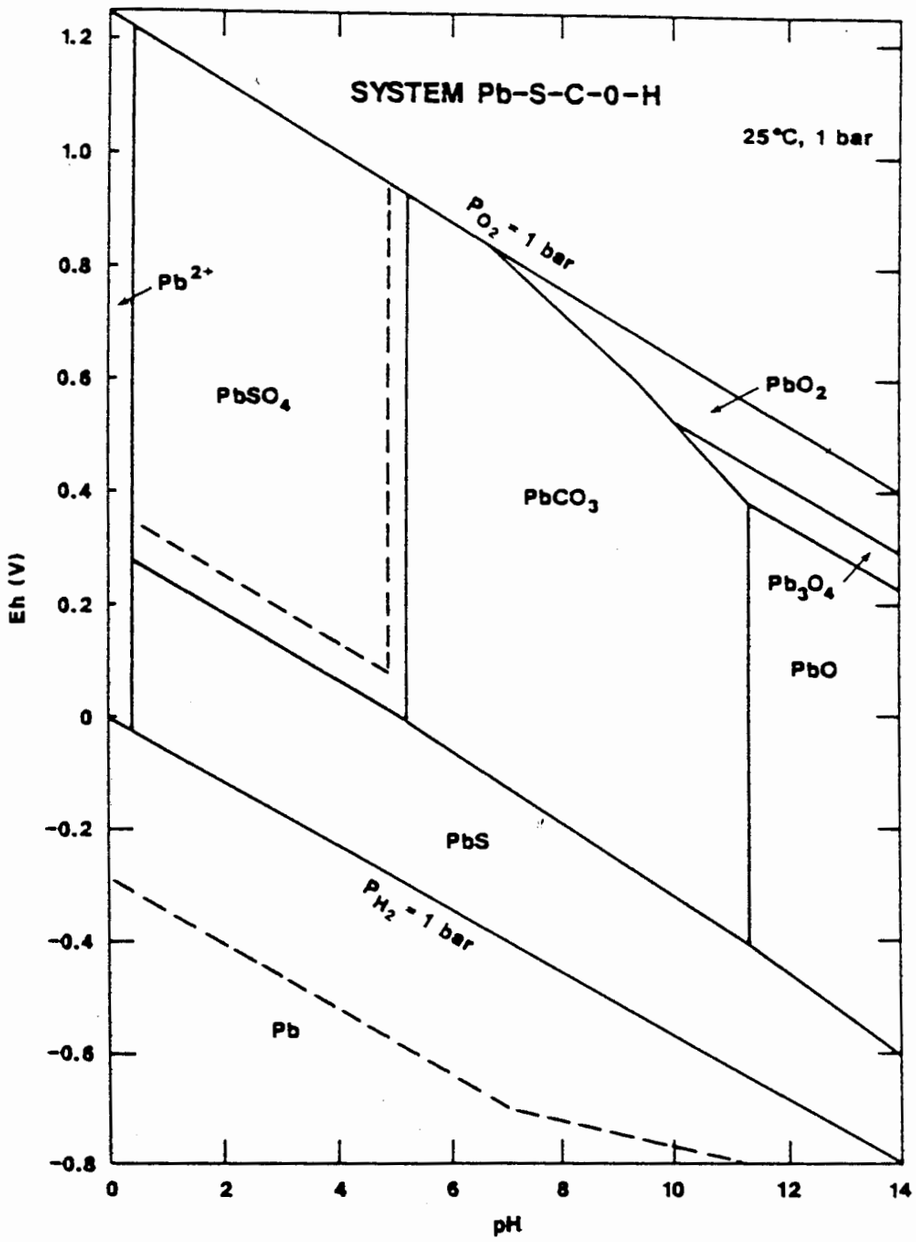


Figure 2.7 Eh-pH diagram for part of the system Pb-S-C-O-H. The assumed activities of dissolved species are : Pb = $10^{-6,-8}$, S = 10^{-3}, C = 10^{-3} (After Brookins, 1988).

(b) *Behaviour of zinc in sediments*

Zinc usually occurs in the +2 oxidation state in sediments. In oxic sediments it will exist as the soluble Zn^{2+} ion (Figure 2.8). In acidic, aerobic environments, Zn has medium mobility and will be in an exchangeable form on clays and organic matter. At higher pH, however, the solubility of Zn^{2+} is lowered by it being chemisorbed on oxides and aluminosilicates, and being complexed with humic substances. Zn mobility in neutral environments is very low, whereas in slightly alkaline conditions Zn-organic complexes can increase the mobility. In strongly alkaline environments, Zn-hydroxy anions can form which increase solubility. In sediments and soils which are contaminated with Zn, the precipitation of Zn oxide, hydroxide or hydroxycarbonate at a pH greater than 6 may limit the solubility of Zn. It is suggested that Zn^{2+} may be able to co-precipitate in the octahedral sites of oxides and silicates (Kiekens, 1995).

In reducing sediments, the mobility of Zn^{2+} may initially be increased due to dissolving Fe and Mn oxides, but Zn mobility is soon limited by the formation of insoluble zinc sulfide minerals (McBride, 1994). An investigation into the variability of dissolved Zn in the Seine Estuary by Boughriet *et al.* (1992) suggested that Zn was mainly influenced by salinity. The concentration of dissolved Zn rose to about 0.17 μM (0.01 ppm) in a salinity range of 3-8 ‰. Thereafter the level of dissolved Zn decreased consistently (to about 0.05 μM or 0.003 ppm) with increasing salinity (>20 ‰). Considering that the salinity of normal seawater is 35 ‰ (Bearman, 1989b), this may have an affect the concentration of Zn in the sediment aqueous phase. It is important to note, however, that the variability in dissolved Zn concentrations found in this study may have been related to tidal disturbances in the estuarine mixing area.

(c) *Sources of zinc contamination*

The main pollutant sources for zinc in sediments and soils are metal mining activities, agricultural use of sewage sludge and compost materials, and the use of agrochemicals such as fertilisers and pesticides (Kiekens, 1995).

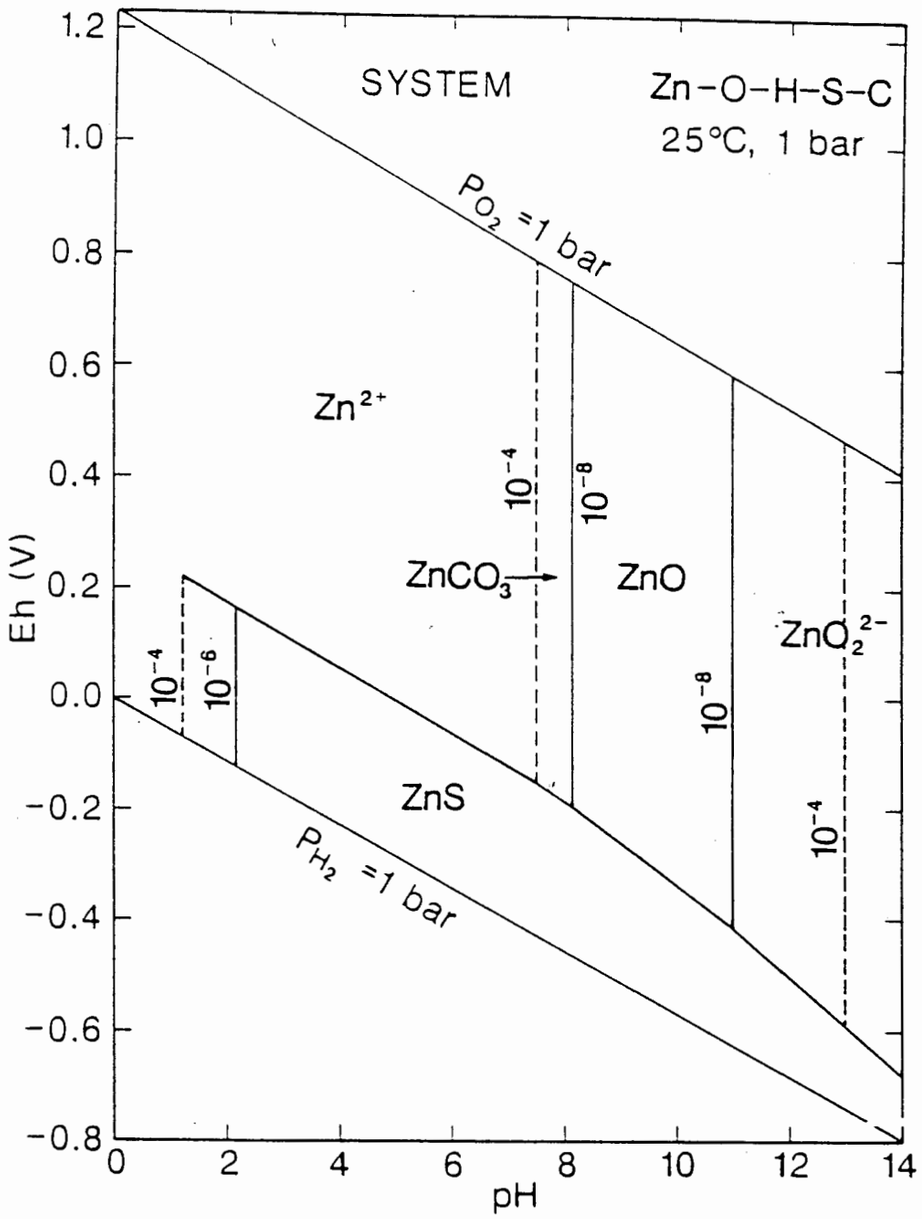


Figure 2.8 Eh-pH diagram for part of the system Zn-O-H-S-C. The assumed activities of dissolved species are: Zn = $10^{-6,-4}$, C = 10^{-3}, S = 10^{-3}.

2.7 The equilibrium partitioning concept

A useful approach for investigating the distribution of trace metals in soils and sediments is the equilibrium partitioning concept (Shea, 1988). The concept assumes that chemical species are in equilibrium with respect to the solid-solution interface. In order to apply this concept, the partition coefficient (K_p) must be calculated. This is defined as,

$$K_p = [Metal]_{solid\ phase} / [Metal]_{pore\ water}$$

The partition coefficient is a measure of the tendency for a metal to be bound to the solid phase (Sung, 1995). Partition coefficients have been used extensively as parameters in metal fate models and risk assessment procedures (Comber *et al.*, 1995; Sung, 1995; Lee *et al.*, 1996; Janssen *et al.*, 1996; Radovanovic and Koelmans, 1998). Using water quality criteria and estimated partition coefficients, maximum permissible metal concentrations for the solid phase can be calculated.

Matters are complicated, however, in that K_p is not a metal-specific constant, but depends on a number of factors such as pH, ionic strength, redox potential, the nature of the adsorbing metal, and the nature of the adsorption phase (including clay minerals, organic matter and the oxyhydroxides of Fe, Al and Mn).

2.7.1 Trace metal partitioning in aquatic systems

There is very little literature available on trace metal partitioning in marine inlets that do not receive freshwater inputs. The majority of the literature concerns the distribution of heavy metals in estuaries and rivers.

Chiffoleau *et al.* (1994) investigated the partitioning of trace metals between the particulate and aqueous phases of surface waters collected in the Seine Estuary. The order of decreasing partition coefficients was found to be Pb > Co > Cu > Zn > Ni > Cd. Lead had the greatest affinity for the particulate phase and cadmium the strongest affinity for the dissolved phase. The sequence of partition coefficients determined by

Chiffoleau *et al.* (1994) is in agreement with that of Balls (1989) for other European coastal waters. In a study conducted by Regnier and Wollast (1993) on the distribution of trace metals (Ni, Co, Cr, Zn, Cu, Cd and Mn) in suspended matter and sediments in the Scheldt estuary, the trace metal distribution was found to be strongly affected by salinity, pH, dissolved oxygen and turbidity. Salinity, in particular, was found to decrease the concentrations of Al, particulate organic carbon (POC), Ni, Cr, Pb, Cd and Cu in the particulate phase.

Similarly, Ekpo and Ibok (1998) report that the levels and distribution of non-detrital Fe, Mn, Cu and Pb in surface sediments of the Calabar River (South Eastern Nigeria) are significantly influenced by physico-chemical changes (salinity, dissolved oxygen and conductivity) in the overlying water. Balls (1989) however, maintains that in areas where the salinity is greater than 20 ‰ (i.e. tending towards the salinity of average seawater), variations in partition coefficient trends are not greatly influenced by physico-chemical factors, such as salinity, pH and turbidity. Regarding studies of metal partitioning in surface waters, it is important to note that suspended particulate matter is more sensitive to immediate changes in physico-chemical conditions than is sediment.

2.7.2 Possible approaches to predicting partition coefficients

(i) *Empirical approach using statistical relationships*

This method describes K_p in terms of the sediment system parameters. It requires that the sediment samples cover a range of conditions and compositions. Pore water is extracted from the solid phase and metal concentrations in both portions are determined. These data are used to calculate partition coefficients. Solid phases are characterised fully in terms of dominant sorption phases and pH. Multivariate statistical analyses are performed to determine statistical relationships between observed K_p values and sediment parameters. This allows the partition coefficients to be expressed in terms of regression equations, which incorporate sediment parameters and corresponding weighting factors. Van den Hoop (1995) and Janssen *et al.* (1996) provide examples of this approach.

(ii) *Fundamental approach using a chemical model*

The equilibrium speciation of a system can be calculated using computational procedures that are based on thermodynamic principles. Requirements for setting up a chemical equilibrium model include (a) knowledge of the chemical reactions that take place in the system; the equilibrium constants for each of these chemical reactions, (b) the total concentrations of the components taking part in the reactions, and (c) the parameters defining the state of the system, such as, pH, temperature and redox potential (Pretorius *et al.*,1996). Adsorption reactions are modelled as surface complexation reactions. This means, that the adsorption of cations is viewed as taking place at specific sites and the co-ordinating surface functional groups are regarded as complexant ligands. The advantage of this approach is that adsorption reactions can easily be incorporated into the thermodynamic framework used for aqueous phase complexation (Pretorius *et al.*,1996).

According to Pretorius (1997), the thermodynamic approach is more suitable for predictive purposes, as the empirical method is restricted to being applied over its calibration range only. There are, however, also problems associated with the former approach. These problems are related to (a) the reliability of the equilibrium constants, (b) the description of the adsorption behaviour of organic ligands in natural systems, and (c) the description of the adsorption behaviour of adsorption phases in natural environments (Pretorius *et al.*,1996).

Various numerical models, such as the one developed by Ng *et al.*(1995), have made use of partition coefficients to predict the fate of contaminants in aquatic systems. This group devised a geochemical programme based on empirical partition coefficients and using a hydrodynamic model, to simulate the tidal distributions of Cd and Zn in the Humber estuary

2.8 Conclusions

The processes highlighted as being responsible for limiting the mobility of trace metals in sediments include precipitation and co-precipitation, adsorption, complexation and

the incorporation of metals into crystal lattices.

The alkaline pH of seawater is conducive to the adsorption of trace metals onto Fe and Mn oxyhydroxides, clay minerals and organic matter. Fe and Mn oxyhydroxides are particularly important adsorption phases in oxic sediments. In an oxidising environment and at pH 8.2, the stable iron phase is likely to be $Fe(OH)_3$ and various polymorphs of MnO_2 will probably be present. The pH of seawater and a moderate Eh make it possible for Mn^{2+} (aq) to exist.

In the anoxic sediments (at an Eh below the sulfide-sulfate boundary), sulfide minerals (particularly those of iron) are sure to play an important role in controlling trace metal mobility. The dominant Fe-sulfide mineral is likely to be pyrite (FeS_2). This is the most thermodynamically stable Fe-sulfide under alkaline, reducing conditions. However, metastable forms such as amorphous FeS, mackinawite (FeS) and greigite (Fe_3S_4) may also contribute to the iron sulfide fraction. Mn may be present as MnS under these conditions. The concentration of the AVS in a sample shall serve as an indication of how reduced the sediment is.

Cadmium is made mobile in oxic, alkaline sediments by the formation of $CdCl_2$ and Cd-hydroxy species, as well as soluble Cd-organic complexes. The major adsorption phases acting to remove Cd from solution are $Fe(OH)_3$ and humic substances. Cd also tends to co-precipitate with carbonate minerals. In anoxic marine sediments, most of the Cd will be in the form of CdS.

The mobility of Cu is increased by the formation of soluble hydroxy, carbonate and organic complexes. Copper solubility in oxic sediments can be reduced by adsorption of the metal onto Fe and Mn oxyhydroxides and organic matter (particularly the latter). In reducing sediments, most of the copper will be associated with Cu_2S, and to a lesser extent with CuS.

Lead can be removed from the sediment aqueous phase (under alkaline and oxic conditions) by precipitating as a carbonate, hydroxide or phosphate, by complexing with humic substances, and by being adsorbed onto oxides (especially Mn-oxides)

and clays. Lead solubility is increased by the formation of soluble Pb-organic and Pb-hydroxy complexes. Under reducing conditions Pb exists as the highly insoluble mineral PbS.

In oxic marine sediments zinc can exist as Zn^{2+}(aq) as well as in the form of soluble hydroxy, carbonate, organic and chloro-complexes. At the pH of seawater however, the solubility of Zn can be reduced by sorption on Fe and Mn oxyhydroxides and clay minerals, and complexation by humic substances. The formation of insoluble Zn sulfides in anoxic sediments limits Zn mobility.

Unlike in estuary and river systems, the physico-chemical conditions in Saldanha Bay (especially pH and salinity) are likely to be fairly constant. Hence, it is expected that the heavy metal partition coefficients will be influenced mainly by the concentrations of Fe, Mn and Al oxyhydroxides, sulfide content, organic carbon content and the amount of clay present in the sediments.

CHAPTER 3

Geochemistry of the sediment solid phase

3.1 Introduction

The surface layer of a sediment is an area of intense biogeochemical activity. This portion of the sediment also plays an important role in the cycling of elements in the marine environment and directly affects the quality of the overlying water through the exchange of solutes. Trace metals concentrated in surface sediments constitute a potential danger for the organisms in the system. In order to understand the factors controlling the mobility of trace metals in the sediments of Small Bay, it is essential to have a thorough knowledge of the geochemical characteristics of the sediments. This information can be used with previous studies on the sediments of Saldanha Bay to assess the changes occurring in the system.

The purpose of this chapter is to provide, as far as possible, a qualitative as well as quantitative geochemical characterisation of the sediments in Small Bay, Saldanha Bay. It describes the sampling procedures, the steps taken to prepare the samples for analysis and the analytical techniques used in the characterisation. Focus is placed on aspects of the sediment solid phase which are likely to have a significant influence on the mobilities of Cd, Cu, Pb and Zn in the sediment system.

3.2 Sampling

Sediment core samples were taken during a week-long sampling trip (3 - 7 August) in 1998. Core samples were collected from a total of 17 sites in Small Bay. A team of divers extracted two core samples at each location. Sampling sites were pre-selected with the aid of a Geographical Information System, and a Global Positioning System was used in the field. The locations of all sampling sites are shown in Figure 3.1.

Samples were collected in cylindrical PVC (polyvinyl chloride) corers, 50 cm in length and 12 cm in diameter. The corers were depressed into the sediment by hand and

sealed underwater with PVC end-caps.

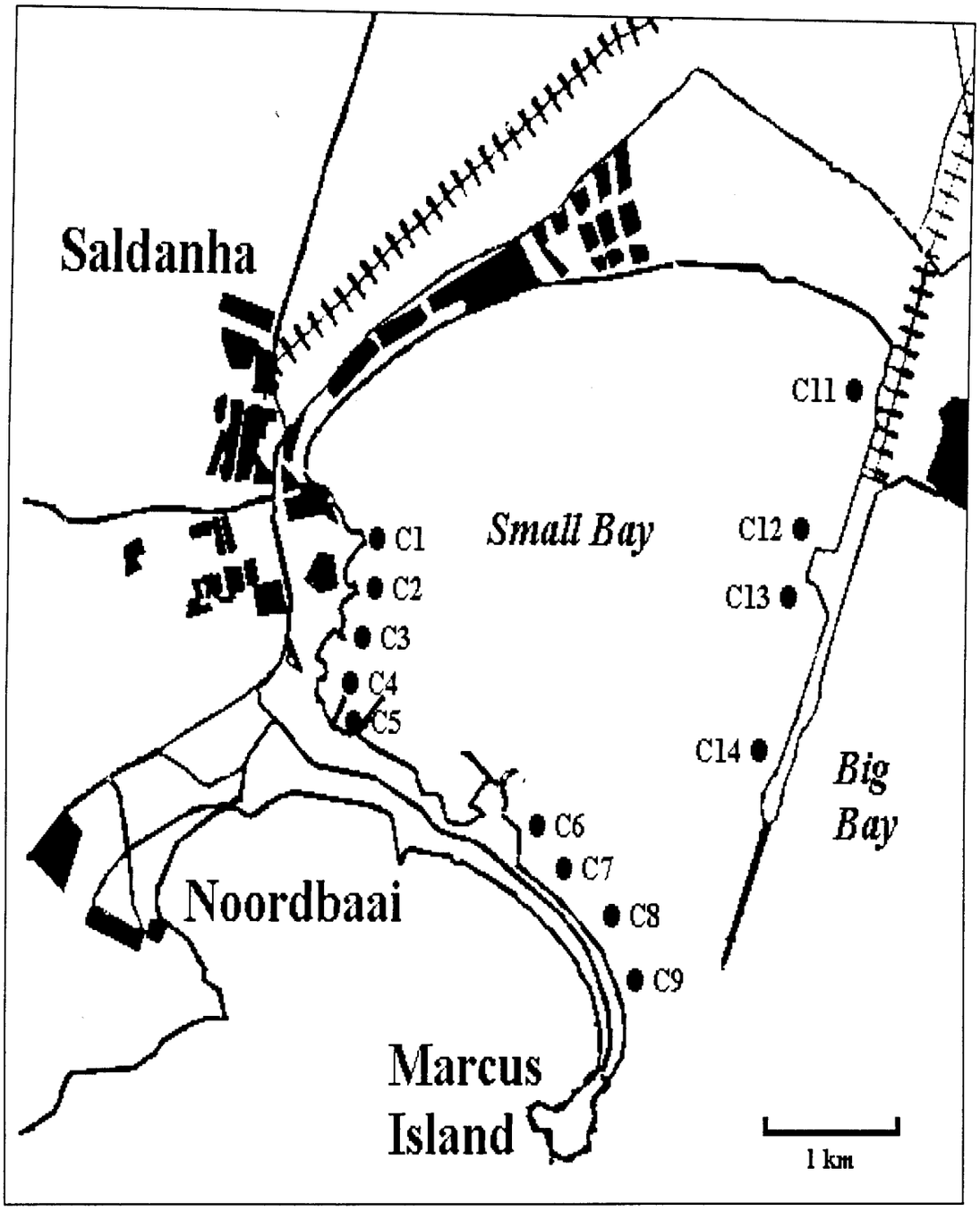


Figure 3.1 Locations of sampling sites in Small Bay.

This ensured a minimum of contamination and prevented the loss of the finer fractions of the sediments. The core samples were frozen in a temporary storage facility in Saldanha Bay and transported, at room temperature, to a laboratory freezer before sample preparation. The cores were kept upright at all times to minimise vertical mixing.

3.2.1 Sample numbers

Although core samples were collected from 17 sites in Small Bay, only 13 of these samples were selected for analysis and used in the project. Samples were selected according to their locations in the Bay and their sediment length. It had been predicted that a pore water volume of 1.2 L per site would be necessary to allow for complete characterisation of the aqueous phase. Hence, it was essential to select samples which contained an adequate amount of sediment. Samples were selected from the three areas of concern and importance in Small Bay: the zone adjacent to the iron ore jetty; the zone adjacent to the fish factories; and, the zone containing the mussel rafts. The cores chosen for analysis were cores C1 to C9 and C11 to C14.

3.2.2 Physical description of the sediment cores

Visual inspection of the cores revealed that the majority of them were homogeneous with respect to colour and texture, while some cores exhibited gradual changes in colour and particle size down their lengths. The heterogeneous cores were characterised by dark organic mud at the top and lighter sand below. None of the cores showed distinct boundaries between layers. Most of the samples collected in the fish factory region (C1-C5) and the mussel bed area (C6-C9) contained substantial but varying amounts of organic matter and some produced strong smells of H_2S when extracted from the PVC corers. Large shell fragments were found in most of the dark organic-rich samples.

The cores from the jetty region (C11-C14) consisted mostly of sand, some with black mottling. Sample C14, however, was predominantly clay and contained very little sand. Particle size data are unfortunately not available to verify the sediment texture

descriptions. Table 3.1 contains descriptions of the sediment samples in terms of their colour, texture and smell.

Table 3.1 Sediment sample descriptions

Sample	Sediment colour, texture and smell	*Average core length (cm)
C1	Homogeneous; black mud containing mussel shells; strong smell of H_2S	15.5
C2	Dark green/black muddy sand at top; green/grey muddy sand at bottom	29.5
C3	Black organic matter (fish debris) at top; fine green/grey sand at bottom	32.5
C4	Homogeneous; dark green fine mud; occasional shell fragments	21.5
C5	Homogeneous; dark green/black mud containing mussel shells; strong smell of H_2S	15.5
C6	Homogeneous; green/grey mud containing mussel shells; strong smell of H_2S	34
C7	Homogeneous; black mud containing coarse shell fragments at the bottom; strong smell of H_2S	16
C8	Homogeneous; fine khaki sand	20
C9	Homogeneous; fine green/grey sand containing large sand prawns	27
C11	Homogeneous; fine light brown sand with grey mottling	28
C12	Homogeneous; light grey sand	42
C13	Light brown muddy sand at top; fine grey sand at bottom containing shell fragments	29
C14	Homogeneous; light grey mud with black mottling	47.5

*Average length of the two sediment cores obtained at each site.

The divers experienced some difficulty in depressing the PVC corers fully into the sediment and as a result, the majority of the cores were not filled with sediment sample. The cores ranged from 15 to 50 cm in length. Due to the fact that trace metals are usually concentrated in the top few centimetres of the sediment and that the core samples were homogenised before analysis, the variations in core length will have resulted in dilution of trace metal concentrations in the samples of greater volume.

3.2.3 Sample handling and preparation

Frozen sediments were extruded from the PVC corers by removing the end-caps and pushing at the bottom end with a polyethylene container. The frozen and intact sediments were inspected and described in terms of colour, texture and odour. The length of each core was also recorded. This process was carried out as quickly as possible to minimise oxidation of anoxic material. If the core contained a frozen portion of overlying water at the top end, this was removed with a stainless steel knife, sealed in a plastic bag and returned to freezer storage. The frozen sediments were cut into 5 cm slices using a stainless steel knife, and individually sealed in plastic bags. The frozen slices were kept in freezer storage until being required for squeezing to remove the interstitial water.

The frozen sediment slices were allowed to thaw in a fridge facility (at 4 °C) before squeezing. An aliquot of approximately 10 g of unsqueezed sediment was collected from the first sediment slice (i.e. surface sediment) to be used in the AVS analysis. This portion was removed immediately and kept in a sealed plastic container in a fridge to minimise oxidation of the reduced material. Sufficiently small containers were used so that they could almost be filled with sediment, thus reducing the amount of air being trapped with the sediment. The sediment sub-sampling procedures are illustrated in Figure 3.2.

Five gas-operated squeezers were used to extract the interstitial water. The squeezers (described by Reeburgh, 1967) use gas pressure (either argon or nitrogen)

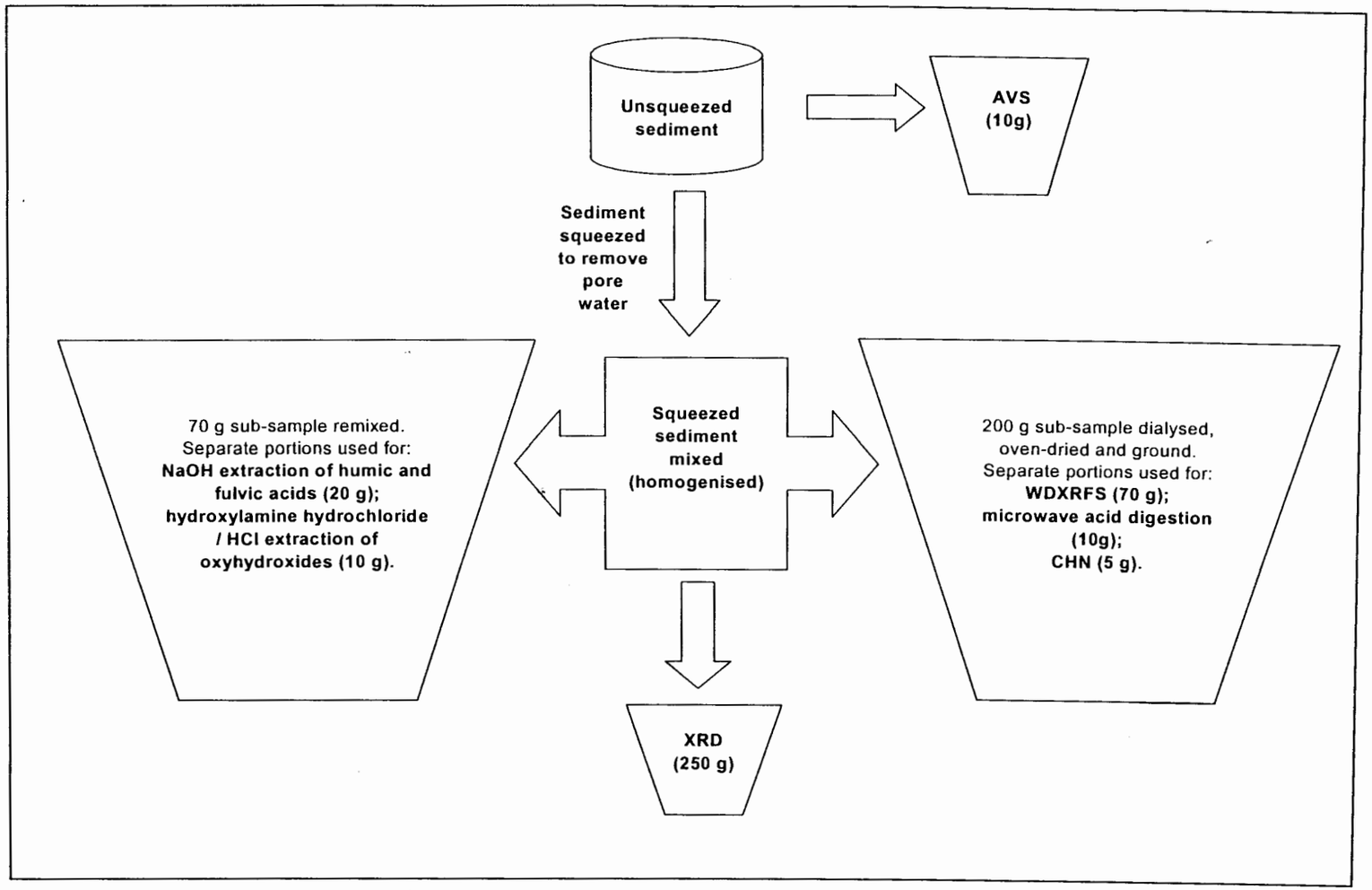


Figure 3.2 Procedure of sediment sub-sampling for analysis

to act against a latex diaphragm and compress the sediment, forcing the interstitial water through filters into a conical flask. The squeezers were operated on a laboratory bench at room temperature. Owing to the size of the squeezing system, it was not possible to carry out the task in an inert atmosphere inside a glove box. Measures were taken however, to minimise the exposure time of the sediment to the atmosphere.

Squeezed sediment samples were used for all the chemical analyses except the acid volatile sulphide (AVS) analysis, where unsqueezed sediment was used. In order to obtain mass for dry weight, the samples were oven-dried (110 °C) for 24 hours. These data were used to calculate dry weight concentrations. Further details of the pore water collection are given in section 4.3.

The squeezed sediment was mixed in a plastic bowl to homogenise it. The plastic bowl had been washed thoroughly in deionised water. A sub-sample of approximately 200 g was remixed and stored in a fridge at 4 °C for use at a later stage. This sub-sample would later be dialysed, oven-dried (110 °C) and finely ground. From this 200 g ground sample, a 70 g portion would be used for wavelength dispersive X-ray fluoresence spectrometry (WDXRFS), 10 g for the microwave acid digestion and another 5 g aliquot for CHN analyses. It was critically important that the WDXRFS and microwave digestion analyses be performed on the same homogenised sub-sample (although different aliquots) to allow for comparison of the two sets of solid phase metal concentrations.

A second sub-sample of about 70 g of bulk sediment was homogenised further and stored in a fridge at 4 °C. From this sub-sample, a 20 g portion would be used for the NaOH extraction of humic and fulvic acids, and another 10 g aliquot would be used for the hydroxylamine hydrochloride / HCl extraction of Al, Fe and Mn oxyhydroxides.

3.3 Analytical methods

Brief descriptions of the analytical procedures used to characterise the sediment solid phase are given below. Details of the methods can be obtained from the respective

references. All chemical analyses except the WDXRFS and XRD were carried out at the CSIR (Council for Scientific and Industrial Research) in Stellenbosch. WDXRFS and XRD were performed in the Department of Geological Sciences, University of Cape Town.

To ensure the accuracy and precision of some of the analyses, certain samples were analysed in duplicate and in most cases, standard reference materials were used. The details of these procedures are presented in Appendix B.

3.3.1 Total element analysis by wavelength dispersive X-ray fluoresence spectrometry (WDXRFS)

Bulk element analysis of major and trace elements in the sediments was carried out by WDXRFS using a Philips PW 1480 X'Unique II X-ray spectrometer. Major elements were analysed in fusion discs and trace elements were analysed in powder briquettes.

A 200 g portion of squeezed sediment was dialysed to remove chloride from the sample. The sample was placed inside a section of dialysis tubing which was kept in stirred distilled water for six hours, after which the distilled water was changed and the sample was left to dialyse for another 24 hours. The sediment was then oven-dried (110 °C) for 4 hours and ground in a carbon-steel Siebtechniek swing mill for 3 minutes to produce a fine powder (-300# or < 70 μm particle size). Approximately 70 g of this powder was set aside for the making of the powder briquettes and fusion discs. Powder briquettes were prepared by mixing 8 g of sediment powder with 2 g of Hoechst wax C in a Turbula mixer mill for 20 minutes, before being pressed into a 30 mm diameter briquette under 10 tons of pressure.

Portions of the remaining oven-dried and ground sediments were oven-roasted to produce fusion discs. For the purpose of summing major element percentages, the water content and "loss on ignition" (LOI) of each ground sample were determined gravimetrically. The ground samples were re-dried in the oven (110 °C) for 4 hours to determine the water content, and subsequently heated stepwise to 1000 ° over a

4 hour period. The samples were left to roast at this temperature overnight. An accurately weighed 0.7000 g portion of oven-roasted sample was mixed with 6 g Sigma 57:43 lithium tetraborate: lithium metaborate flux to make the fusion discs.

The major element sulfur was analysed on fusion discs as well as powder briquettes. The fusion disc determination represents "residual sulfur" or sulfur that remains after the roasting process. Briquettes were also used so that total sulfur could be determined. This includes the volatile and organic sulfur that is lost by roasting to 1000 °C. Briquettes used for total sulfur determination were made without wax because the wax contains a significant amount of sulfur.

3.3.2 Metals extracted by microwave acid digestion (nitric acid, perchloric acid, hydrogen peroxide)

According to Jones and Laslett (1994), the microwave acid digestion method extracts the trace metals that are readily available and not the total metal content of the sediment, since crystalline silicates which may contain metals are not completely dissolved.

From a 10 g aliquot of dialysed, oven-dried and ground sediment (these steps are detailed in section 3.3.1), a quantity of 0.25 g was weighed out accurately for the microwave acid digestion. A 5 mL aliquot of concentrated HNO_3 was added to the 0.25 g of sediment powder, followed by 1 mL $HClO_4$ (60 %) and 1 mL H_2O_2 (30 %). The sample was digested in a Milestone M/S 1200 Mega Microwave oven at 250 W for 30 minutes. A 1 mL aliquot of a La/Cs mixture (lanthanum III oxide, cesium chloride and AR grade nitric acid were used to obtain a mixture containing 10 g/L La, 5 g/L Cs and 200 mL/L HNO_3) was added and the solution was made up to 10 mL in a volumetric flask. The metal concentrations (Al, Fe, Mn, Na, K, Mg, Ca, Cd, Cu, Pb and Zn) were determined by flame atomic absorption spectrophotometry (FAAS).

3.3.3 Organic carbon, nitrogen and hydrogen analysis

Organically bound carbon, nitrogen and hydrogen were determined using a Carlo Erba Elemental Analyser 1106.

From the 5 g of dialysed, oven-dried and ground sediment powder (these steps are detailed in section 3.3.1), 200 mg was weighed out in triplicate into pre-weighed 20 mL clean scintillation vials. An aliquot of 5 mL organic-free 1 M HCl was added to each vial. The samples were agitated in an ultrasonic bath at room temperature for 5 minutes and then dried overnight to remove the inorganic carbon fraction and leave the organic carbon fraction behind.

The equilibrated and re-weighed samples were dropped at preset intervals into a vertical quartz tube, which was maintained at 1030 °C and had a constant through-flow of helium. The flow of helium was temporarily enriched with pure oxygen when the samples were introduced, causing flash combustion. Quantitative combustion was achieved by passing the mixture of gases over chromium oxide (Cr_2O_3). The mixture of combustion gases was then passed over a copper:quartz (5:1) mixture at 650 °C to remove the excess oxygen and to reduce nitrogen oxides to nitrogen. From there the gas mixture passed through a chromatographic column of PorapakQS, heated to 100 °C. Individual components were then separated and eluted as N_2, CO_2 and H_2O. These components were measured by a thermal conductivity detector, connected to an EAGER 100 software computer program. This technique is described in Grasshoff *et al.* (1983).

3.3.4 Hydroxylamine hydrochloride / HCl-extractable metals

The amorphous Al, Fe and Mn oxyhydroxide fractions were extracted using a hydroxylamine hydrochloride / HCl mixture, based on the method described by Hall *et al.* (1996). A 10 g portion of squeezed sediment was mixed to improve homogenisation. From this sediment, a 2 g aliquot was accurately weighed for the extraction. The procedure involved adding 20 mL of a 0.25 M $NH_2OH.HCl$/0.25 M HCl solution to the 2 g of sediment and heating the mixture on a water bath at 60 °C for 2 hours. The suspension was centrifuged for 10 minutes at 5000 rpm and the

supernatant was filtered through glass microfibre filters. Concentrations of Al, Fe, and Mn were determined by FAAS.

3.3.5 Acid volatile sulfides (AVS) and simultaneously extractable metals (SEM)

AVS and SEM are operationally defined methods for the analysis of sulfide and associated metals in aquatic sediments. This method is based on the procedure described by Allen *et al.* (1993).

The volatile sulfides were released by adding approximately 30 mL of 6 M HCl to a mixture of 5 g unsqueezed sediment and 100 mL deionised water in a sealed volumetric flask. A silicone anti-foaming agent was added to control the frothing of the solution. The flask was kept on a magnetic stirrer at room temperature and purged with nitrogen gas for two hours. A Na_2SO_3 scrubber was placed in the gas inlet to remove oxygen from the N_2 and prevent oxidation of the sulfides. The released H_2S was trapped in a zinc acetate solution, forming zinc sulfide. The sulfide concentration was determined by means of an iodometric titration (Standard Methods, 1995). Metals dissolved in the HCl solution constitute the simultaneously extractable metals. This solution was filtered through a 0.45 μm filter before being analysed for Fe, Mn, Cd, Cu, Pb and Zn by FAAS.

3.3.6 Organic carbon content of sodium hydroxide extractable humic and fulvic acids

The humic and fulvic acid fractions of sediments are characteristically soluble in basic solutions. These fractions were extracted from the sediment samples using NaOH, according to the method described by Fu *et al.* (1992).

A 200 mL volume of 0.5 M NaOH was added to 20 g of squeezed sediment. The system was purged with nitrogen, sealed with parafilm, and stirred for 12 hours using a magnetic stirrer. The suspension was transferred to centrifuge tubes and centrifuged for 10 minutes at 5000 rpm. The supernatant was filtered through 0.45 μm

filters and the precipitate was discarded. The supernatant containing the dissolved humic and fulvic acids was analysed for organic carbon.

The technique used is based on the persulfate-ultraviolet oxidation method described by Standard Methods (1995). The organic carbon was oxidised to carbon dioxide by persulfate in the presence of ultraviolet light. Carbon dioxide produced was passed through a semi-permeable membrane into a lightly buffered carbonate/bicarbonate mixture containing phenolphthalein solution. The intensity of the coloured solution was measured in a colorimeter in a flow cell. Potassium hydrogen phthalate standards of known organic carbon content were used to calibrate the concentrations of organic carbon in the interstitial water samples.

3.3.7 Metals using flame atomic absorption spectrophotometry (FAAS)

The total elemental concentrations of the metals in the sediment extracts were determined by means of FAAS. All extracts were filtered through a 0.45 μm Nucleopore membrane filter, and some were diluted with deionised water before being analysed on a Varian AA-1475 flame atomic absorption spectrophotometer.

Blank solutions were used in all cases and the certified reference material, PACS-2, was used for quality control. (PACS-2 is a marine sediment reference material used for the analysis of trace metals and other constituents. It is produced by the National Research Council of Canada).

3.3.8 Clay fraction mineralogy by X-ray diffraction (XRD)

The clay fractions of selected samples were analysed by XRD. In order to isolate the clay fraction from the sand and silt components, the sediment slurries were brought to pH 9 by the addition of 1 M NaOH and mechanically shaken for 4 hours. Thereafter they were transferred to pH 10 Na_2CO_3 solutions. After dispersion the suspension was allowed to settle and the clay sized particles (<2 μm) were siphoned off. The settling and siphoning procedures were repeated until enough clay had been collected. The pH of the decantate was dropped to <7 (but not <5) by using HCl, and NaCl was added to promote flocculation. The flocculated clay was desalinated in

dialysis tubing and the suspension concentration was adjusted to approximately 20 mg/mL.

Clay suspensions were either dried on glass slides or ceramic discs for analysis. In the case of the glass slides being used, 2 mL aliquots of suspension were pipetted onto the slides and allowed to dry slowly at room temperature. The ceramic discs were covered in a thicker layer of clay (about 2 mm in thickness), requiring approximately 10 mL of clay suspension. In order to prevent curling and cracking of the clay layer, the ceramic discs were analysed by the diffractometer before complete drying had occurred.

X-ray diffraction was performed using Cu Kα radiation (λ=1.542 Å) in a Philips PW 1050/37 vertical goniometer controlled by PW3710 electronics. The clay samples were scanned over a range of 4-70 degrees in steps of 0.05 degrees 2θ and 1 s counts. Identification of species from the diffractograms is based on the positions of the lines (in terms of degrees 2θ) and their relative intensities. Mineral identification is empirical. A data file (JCPDS, 1980) is used to associate measured d-spacings and intensities with specific minerals.

3.4 Results and discussion

The following section contains the results of the analytical procedures and geochemical interpretations thereof. The raw data for some of the laboratory analyses are contained in Appendix C. All sediment concentrations reported in this chapter refer to sediment dry weight (110 °C).

3.4.1 Statistical appraisal of data

The geochemical investigation of the sediment solid phase has been aided by the use of statistical analyses. The results of some of these analyses are discussed in this chapter. In order for the statistics results to be regarded with the appropriate degree of certainty, it is necessary to give a statistical evaluation of the analytical data. An appraisal of the use of the analytical data for statistical use is given below.

The sediments were not collected from Small Bay (the population) in a random manner and neither were the cores that were selected for analysis chosen in a random fashion. Therefore, the sample of sediments is biased. It is also important to note that a sample of more than 13 sediment cores would usually be required to provide a refined picture of the nature of the sediment population in Small Bay.

Normal probability plots were prepared to test whether or not the sediments had been drawn from a population with a normal distribution. The majority of the variables were not normally distributed. Since parametric statistics require normality of the data the non-parametric Spearman's rank correlation coefficient was used in this chapter to investigate correlations between the variables. This non-parametric method makes no assumptions with regard to the distribution of the parent population.

A property referred to as "constant sum closure" is displayed by data which represent a proportion of the whole. This refers to variables whose concentrations are reported as percentages (e.g. major element data) and ppm or ppb (e.g. trace element data). The problem of closure is that it invalidates the use of the usual Null Hypothesis that the population correlation coefficient is zero ($H_o : \rho = 0$) as a test to see if two variables vary independently of one another. It is therefore important to realise that there is a problem with significance tests for correlation coefficients calculated from closed data sets. There is no completely satisfactory way of evaluating the strengths of correlations between variables in closed data sets. Nevertheless, as long as the correlation coefficient is used only as a sample descriptor, no serious problems will surface (pers. com. A. Duncan).

3.4.2 Redox status and sulfide content

Much of the sedimentary environment of Small Bay is anoxic. Anoxia is a condition where no dissolved oxygen is available and occurs in natural waters when the consumption rate of oxygen exceeds the supply (Chester, 1990). This first became apparent during the visual inspection of the frozen cores when some samples were noted as being black or dark green in colour, having a high organic matter content or smelling strongly of H_2S. Further evidence arose during the sample preparation

procedures when colour changes were observed. Exposure of the sediment samples to the atmosphere caused the surfaces to change to a lighter colour (usually a grey or brown). The colour change took place to a depth of approximately 1.5 cm, while the inside of the cores showed no colour change. This was first observed when the slightly thawed sediment cores were sliced in preparation for the squeezing process. It is suspected that the oxidation of reduced material took place over a period of a few hours as the frozen cores were allowed to thaw. Once the sediment slices were sealed in plastic bags and returned to the fridge for temporary storage the rate of oxidation was reduced but not halted altogether. As a general approximation, the rate of a reaction doubles for every 10 °C increase in temperature (Ebbing, 1987).

The sediments were treated with cold hydrochloric acid to determine the concentration of AVS, which is composed mainly of amorphous, iron monosulfide $FeS_{(s)}$. This mineral is responsible for the black colour of anoxic sediments and is in equilibrium with aqueous phase sulfide by the reaction:

$$FeS_{(s)} \leftrightarrow Fe^{2+} + S^{2-}$$

Divalent metal ions such as Cd^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} react with solid AVS to form precipitates that are very insoluble in pore water (Ingersoll *et al.*, 1997).

$$Me^{2+} + FeS_{(s)} \leftrightarrow MeS_{(s)} + Fe^{2+}$$

Thus, the iron in $FeS_{(s)}$ is displaced by other metal ions to form Fe^{2+} ions and solid metal sulfide. This displacement occurs because the metal sulfide solubilities of CdS, CuS, PbS, ZnS etc. are all less than that of FeS (Di Toro *et al.*, 1990). Pyrite (FeS_2) however, does not readily exchange trace metals (Allen *et al.*, 1993).

The concentrations of metals that are simultaneously extracted are termed simultaneously extracted metals or SEM. As long as the molar concentration of AVS in the sediment exceeds the combined concentrations of simultaneously

extractable Cd^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}, these metals will form solid sulfides and have very low pore water concentrations. It can, therefore, be expected that the sediment samples which have very high sulfide content will have low pore water concentrations of these divalent metals.

Table 3.2 contains the AVS and SEM (Cd, Cu, Pb and Zn) concentrations of the sediment samples. The highest AVS concentration was produced from sample C7. This core consisted entirely of black mud. Sample C1 contained the highest concentration of simultaneously extractable Fe, Cd (also in sample C7) and Zn, and was highly anoxic. The greatest levels of simultaneously extractable Cu and Pb were obtained from another highly reduced sample, C5.

The SEM/AVS ratio, expressed as the molar sum of the metals (Cd, Cu, Pb, Zn, Hg and Ni) and the molar concentration of acid volatile sulfide, is often used to assess the mobility of the extractable metals in sediments. For SEM/AVS <1, no acute toxicity has been observed in any sediment for any benthic organism (De Groot, 1995). If the ratio >1, the mortality of sensitive species increases in the range of 1.5-2.5 μmol of SEM/μmol of AVS (De Groot, 1995).

Considering that the metals Hg and Ni have not been included in calculating the sum of SEM, it is interesting to note that in nearly half of the Small Bay sediment samples, the ratio of SEM to AVS (Table 3.2) exceeds 1. Samples C1, C2, C3, C4 and C11 have ratios greater than 1.5, suggesting that these sediments could adversely affect sensitive marine organisms. Sample C4 has the highest SEM/AVS ratio of 6.09. Samples C6 and C8 are, according to De Groot (1995), close to the range which is dangerous to benthic life.

Owing to the exclusion of Hg and Ni, less can be said about the sediments with ratios below 1, except that some of them have ratios well below 1 (C7, C12, C13 and C14) and others are close to the value of 1 (C5 and C9). Sample C7 has the lowest SEM/AVS ratio of 0.07.

Table 3.2 Concentrations (μmol/kg) of acid volatile sulfides (AVS) and simultaneously extractable metals (SEM) in the sediments.

Sample	AVS	Fe	Cd	Cu	Pb	Zn	SEM	SEM/AVS
C1	662	68953	18	330	257	2485	3090	4.67
C2	181	11746	4.3	73	40	268	385	2.12
C3	179	14073	4.2	76	31	306	417	2.33
C4	162	32050	13	200	90	682	985	6.09
C5	6042	34628	13	483	625	1597	2718	0.45
C6	440	20018	12	52	139	256	459	1.05
C7	8906	30850	18	54	142	414	628	0.07
C8	155	8218	3.6	24	68	86	182	1.17
C9	181	11065	1.7	20	66	47	135	0.74
C11	61	6983	0.9	21	123	49	194	3.18
C12	1526	14270	3.2	28	150	83	264	0.17
C13	3215	13339	2.7	28	198	147	376	0.12
C14	4412	16920	3.9	41	127	193	365	0.08

*SEM = sum of molar concentrations of Cd, Cu, Pb and Zn.

Limitations of the AVS/SEM ratio to attempt to predict the potential bio-availability of metals in sediments include the fact that the metals extracted simultaneously are not necessarily only associated with the acid volatile sulfides. The metals may be adsorbed onto organic matter, oxyhydroxides or the surfaces of clay minerals. The extraction is, however, unlikely to break down silicate lattices. It is possible that a SEM/AVS ratio of less than 1 could be due to the partial oxidation of the sulfides. The iron which is displaced during the formation of the metal sulfide is likely to be scavenged by ligands such as PO_4^{3-} and CO_3^{2-}, which are usually present in high concentrations in anoxic sediments.

According to Cooper and Morse (1998a) the use of HCl-based approaches to investigate metal bioavailability is complicated by the fact that the sulfides of metals

such as Cu, Hg and Ni, do not usually dissolve completely in HCl. Cooper and Morse (1998a) emphasise the need for further investigation of the important mechanisms that control interactions between trace metals and sulfide minerals.

Statistical analysis of the relationships between AVS and the simultaneously extracted metals reveal that AVS is correlated with SEM-Pb at the 99 % confidence level (Spearman's R = 0.69, n=13) and with SEM-Fe at the 95 % confidence level (Spearman's R= 0.58, n=13). This suggests that much of the Pb and Fe in the sediments is associated with the sulfide fraction.

3.4.3 Organic matter

The origin of organic material in the marine environment can either be allochthonous (terrestrial material derived from outside the oceans) or autochthonous (from within the marine system) (Millero, 1996). Terrestrial input enters the coastal waters by rivers or from the atmosphere. River contributions can include naturally derived sources of organic material as well as organic substances derived from sewage and industrial effluent.

Atmospheric input can be wet (liquid) or dry (gas and solid) deposition but it is sometimes difficult to distinguish these categories from each other. For example, liquid deposition (rainwater) can contain particulate material as well as dissolved gases. It is estimated that 2.2×10^{14} g of carbon enters the oceans by rainfall annually (Millero, 1996).

The organic matter in marine aerosols is dominated by waxes of terrestrial origin. These aerosol lipids originate from wind erosion of soils and direct emission from vegetation. The oceans receive more organic material from rain than from dry deposition (Millero, 1996).

The sources of organic matter in Saldanha Bay include primary productivity by marine plankton, excretion by marine organisms (eg. mussel faecal pellets), terrestrial input of fish factory waste and terrestrial input by the atmosphere (both wet and dry

deposition). There is no terrestrial contribution of organic material by rivers to the Bay and surface runoff is very limited.

In studying organic material in aquatic systems, it is common practice to distinguish dissolved organic matter (DOM) from particulate organic matter (POM). The latter is usually operationally defined as those species which are retained by a 0.45 μm filter, although some workers have used filters with pore sizes ranging from 0.40 to 1.0 μm to achieve separation of POM from DOM (Millero, 1996).

The organic matter described as being associated with the solid phase of the Saldanha Bay sediments however, can be defined as the organic material which did not pass through the coarse filter papers (pore size unknown) used in the squeezing process. Hence, some colloidal material (larger than 0.45 μm) would have been removed with the interstitial water (later to be discarded after filtration of the pore water) but this would have constituted a minimal contribution to the total organic matter content of the solid phase. The DOM fraction is discussed in chapter 4.

Figure 3.3 shows the accumulative percentages of organic carbon, nitrogen and hydrogen in the sediment samples. The raw data are tabulated in Appendix C. The range of percent organic carbon in the Saldanha Bay sediments is from 0.31% (sample C13) to 6.90 % (sample C4) and is in agreement with the range given by Chester (1990) for most nearshore sediments (1-5 %). The average organic carbon content is 2.70 % (n=12). Particulate organic nitrogen (PON) and particulate organic phosphorus (POP) in marine sediments are usually present in much smaller quantities than POC (Millero, 1996). Carbon makes up approximately 50 % by weight of marine organic matter and consequently, the total amount of organic matter can be approximated by multiplying POC by a factor of two (Libes, 1992).

Most of the Small Bay sediments contain a larger percentage of POC than PON, except however, samples C8, C12 and C13, which all contain slightly more PON than POC. The range of %N is smaller than that of %C: percentage N ranges from 0.06 % (sample C14) to 1.35 % (sample C8). For all the samples %H is below 1 %. The percentage of POP in the sediments was not determined. It is reasonable to expect

the dark and muddy sediments to have higher organic carbon contents than samples which consist predominantly of light-coloured sand. Generally, this is the case in the Small Bay sediments. It is surprising, however, that samples C2 and C3 (especially the latter) do not have higher percentages of organic carbon, as they are composed almost entirely of green/black mud.

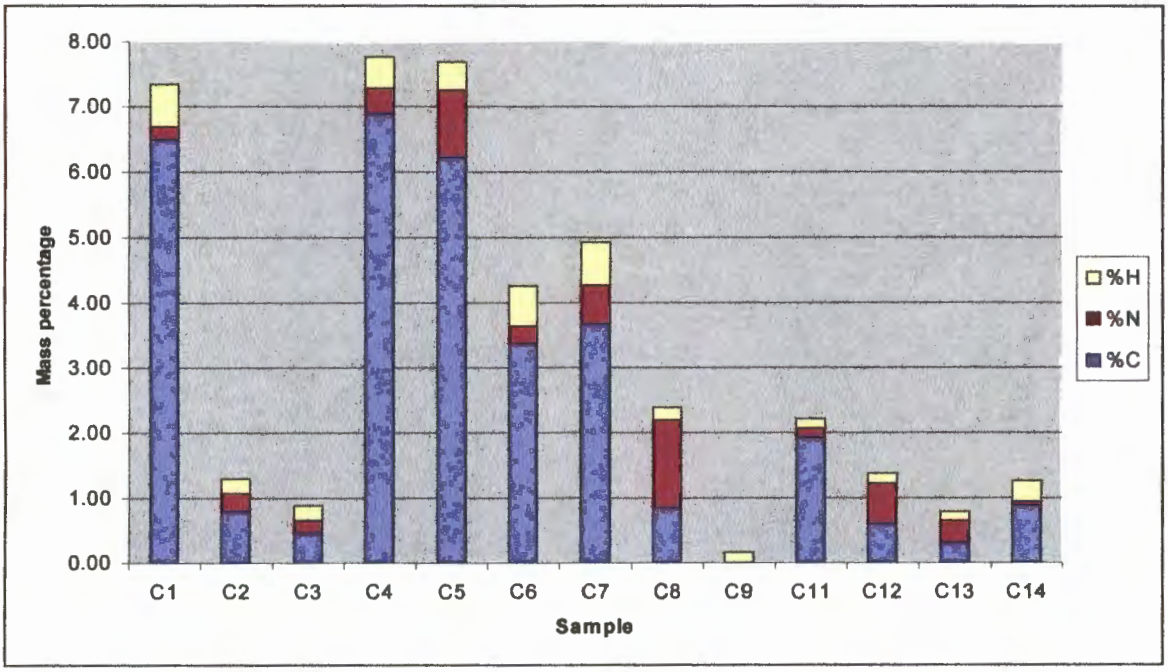


Figure 3.3 Percentages of particulate organic C, N and H in the sediments (% organic carbon and % nitrogen data not available for sample C9)

Much biological activity occurs at the sediment-water interface and therefore, POM that reaches the seafloor is subject to extensive degradation before being buried. The sediment-water interface is heavily populated with microbes and due to the high rate of organic matter decomposition the organic carbon and nitrogen contents of the particulate matter are decreased by an order of magnitude prior to burial (Libes, 1992). This loss continues after burial, but at much slower rates.

The ratios of carbon to nitrogen in the sediment POM are presented in Table 3.3. The ratios vary greatly, ranging from 0.62 (C8) to 35 (C1). An average C/N ratio of 9.5 was calculated for the Small Bay sediments. This value is similar to the C/N statistic of 8.5 available for the organic material at the sediment surface in the Oman Sea (Libes, 1992). The sediments of the Oman Sea have an organic carbon content of approximately 3 %.

Since the protein component of organic material contains significantly more nitrogen (17.8 %N) than lipids or carbohydrates (0.61 and 0 % N respectively) (Libes, 1992), it might be expected that the lowest C/N ratios would be found in the sediment samples collected from the area where fish waste is disposed (C1-C5). Sample C1 however, has the highest ratio of carbon to nitrogen in the POM. The three lowest C/N ratios were found in samples which are composed predominantly of sand (C8, C12 and C13). High C/N ratios may be linked to the fact that nitrogen-rich compounds degrade faster than the nitrogen deficient ones (Libes, 1992; Millero, 1996). The large biopolymers are the first compounds to degrade. Large proteins are decomposed into polypeptides which are in turn broken down into free amino acids. These amino acids are then converted into fatty acids and smaller molecules, including CO_2, CH_4, NH_4^+, HPO_4^{2-}, HS^-, phenols and urea.

Table 3.3 Organic carbon to nitrogen ratios in the sediment POM

Sample	C/N
C1	35
C2	2.8
C3	2.5
C4	18
C5	6.1
C6	13
C7	6.1
C8	0.62
C9	na
C11	14
C12	0.95
C13	0.91
C14	15

C/N ratios calculated from % organic C and N data in Appendix C; na: data not available.

The degradation of lipids produces hydrocarbons, carbohydrates and small carboxylic acids. These components are decomposed further to produce CO_2 and CH_4. Cellulose and starch degrade completely to CO_2 and CH_4 (Libes, 1992). As a consequence of the faster decomposition of nitrogenous compounds, the C/N ratio in sediments increases with depth. For example, the C/N ratio of organic material in the

Oman Sea increases from about 8.5 at the surface to approximately 12 at a depth of 3 m (Libes, 1992).

The top meter of a sediment column however, is usually characterised by chemical homogeneity due to bioturbation (Libes, 1992). It is possible that the variation in C/N ratios in the Small Bay sediments may be due to different degrees of bioturbation and/or re-suspension of organic material at different sites in the Bay.

The sediment samples were treated with aqueous sodium hydroxide to dissolve the humic and fulvic acid fractions. Although this selective extraction leaves the humin component of the humus unextracted, it can provide a relative indication of the amount of organic material available for the adsorption of metals in the sediments. The NaOH extract was analysed for organic carbon (Table 3.4) and these concentrations can be used to represent the levels of humic and fulvic acids in the samples.

Table 3.4 Organic carbon content of sediment humic and fulvic acids

Sample	Organic carbon in fulvic and humic acids (g OC/kg sediment)
C1	2.27 (65)
C2	0.64 (7.9)
C3	0.93 (4.6)
C4	1.66 (69)
C5	1.32 (62)
C6	2.45 (34)
C7	1.79 (37)
C8	0.60 (8.4)
C9	0.50 (na)
C11	0.60 (19)
C12	0.21 (5.9)
C13	0.34 (3.1)
C14	0.36 (8.8)

Concentrations of total organic carbon (g/kg) are given in parentheses; na : data not available

Organic carbon concentrations in the NaOH extracts are considerably less than the total organic carbon determined in the CHN analyses This is obviously due to the fact that the NaOH treatment acts as a partial extraction. Although there is a positive correlation ($p<0.01$) between the two sets of organic carbon data (Spearman's $R=0.72$; $n=12$), the plot of total organic carbon determined in the CHN analyses against the organic carbon in the NaOH extract (Figure 3.4) does not suggest that there is a strong correlation between the two data sets.

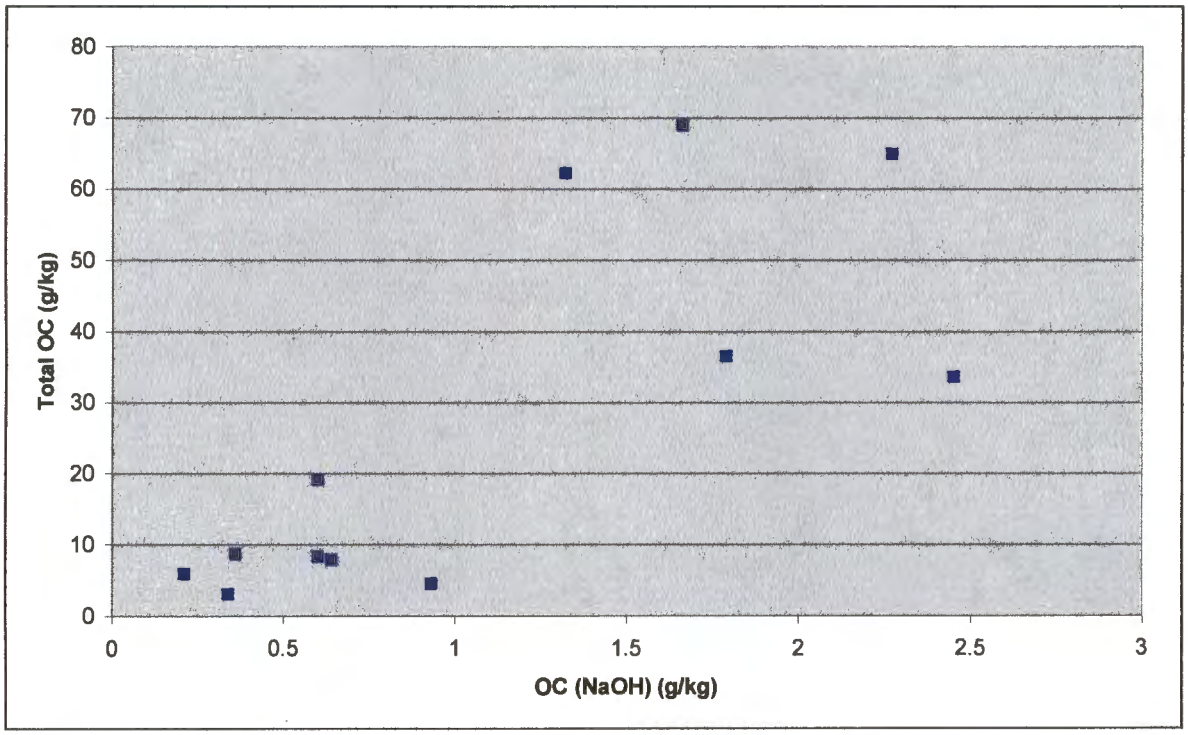


Figure 3.4 Total organic carbon in the sediment solid phase versus organic carbon in the humic and fulvic acid fraction (NaOH extract).

Humic substances consist of mixtures of plant and animal debris at various stages of decomposition and so the chemical composition can vary according to the source of organic input and the environment of the deposition. It is possible that the humic material in Small Bay may vary, depending on whether the organic matter is derived mainly from fish waste, mussel bed waste, seaweed or other sources.

3.4.4 Oxyhydroxides of Al, Fe and Mn

The oxyhydroxides of Fe and Mn, and to a lesser extent Al, have been identified as being the principle adsorption phases for many metals in oxic sediments (Honeyman,

1992; Drever, 1997). Scavenging by these secondary oxides which are present as coatings on mineral surfaces or as individual particles, can occur via several mechanisms such as co-precipitation, adsorption, surface complex formation and inclusion into the lattice.

The amorphous oxyhydroxides of Al, Fe and Mn were extracted from the sediment samples by treatment with hydroxylamine hydrochloride/HCl. The concentrations (mg/kg sediment) of Al, Fe and Mn in this reducible fraction are presented in Appendix C.

Figure 3.5 displays the log concentrations of Al, Fe and Mn in the hydroxylamine extractions in a bar chart.

The concentration of Al ranges widely from 1.16 mg/kg (C12) to 222 mg/kg (C2). This represents a two-order of magnitude difference. Excluding sample C2 and sample C3 (221 mg/kg), the remaining 11 sediments all have Al concentrations less than 25 mg/kg and the average concentration (n=11) is 12 mg/kg.

Like Al, Fe concentrations in the oxyhydroxide fraction range broadly from 6.65 mg/kg (sample C8) to 647 mg/kg (sample C3), with samples C2 (614 mg/kg) and C3 again having the highest concentrations. Of the 13 sediments, nine of the samples have Fe levels below 30 mg/kg and the average (n=9) concentration is 15.5 mg/kg. The highest concentrations of Mn were also found in samples C3 and C2 (3.79 and 3.63 mg/kg respectively).

The statistical relationships between the concentrations of Al, Fe and Mn were investigated: positive correlations exists between Fe and Mn at the 99 % confidence level (Spearman's R = 0.77; n=13) and between Al and Fe at the 95 % confidence level (Spearman's R = 0.57; n=13).

The concentrations of both Fe and Mn oxyhydroxides are determined by the redox condition of the sediment. The association between Fe and Mn may be further explained however, by their tendency to form mixed oxides due to their similar chemical properties and ionic radii (Hall *et al.*, 1996).

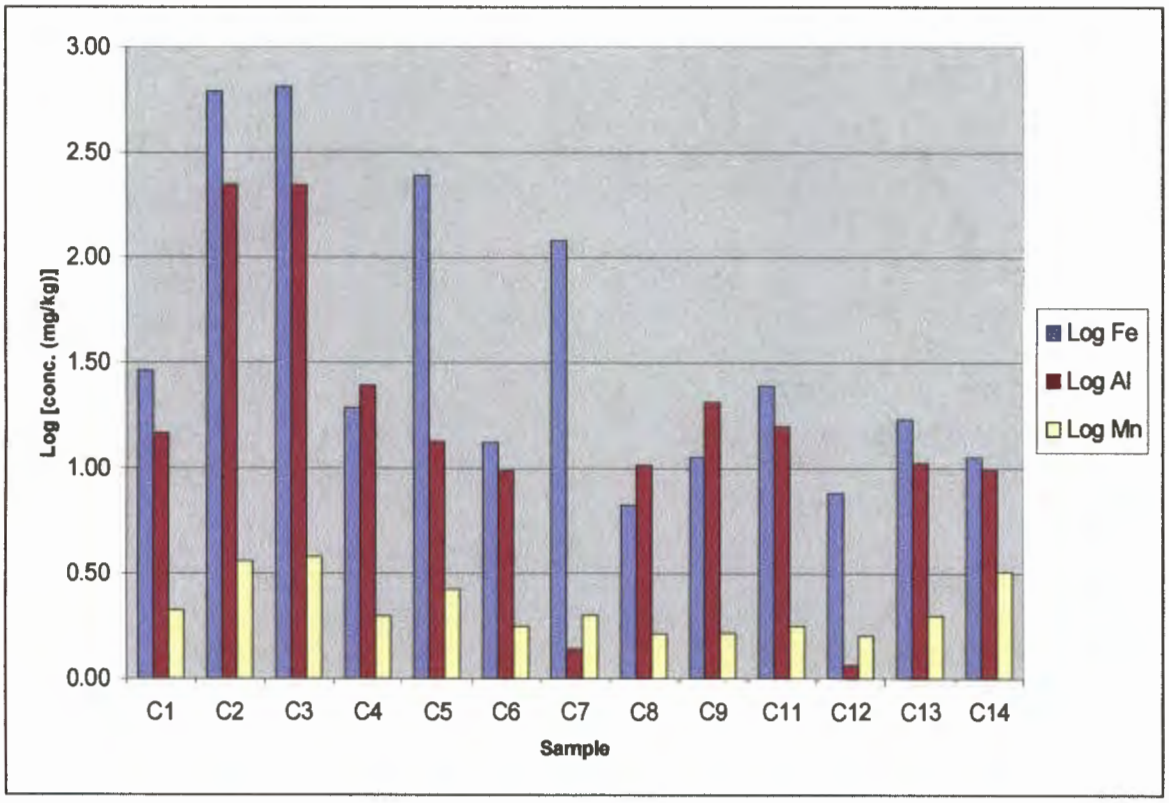


Figure 3.5 Log concentrations of Al, Fe and Mn extracted as hydrous oxides.

There is an occurrence of high concentrations of Al, Fe and Mn in sediments C2 and C3, yet the very dark appearances of these samples would suggest that they contain very little reducible material. The high levels of Al, Fe and Mn in these extractions may be an indication that this method of partial extraction is not entirely selective. In fact, the hydroxylamine hydrochloride/HCl extractions have been found to be less than 100 % selective in extracting the reducible amorphous oxyhydroxides only. Work done by Hall *et al.* (1996) showed that the high concentration of 0.25 M HCl led to significant dissolution of monosulfides such as sphalerite and galena, as well as a significant amount of organic material. It is also highly likely that the acidic extractant would dissolve the carbonate phase of the sediment. Hence, the concentrations of Al, Fe and Mn extracted using this method may not truly reflect the amounts of reducible amorphous oxyhydroxides present in the sediments of Small Bay.

3.4.5 Clay mineralogy

The clay fractions of five sediment samples (C4, C5, C6, C7 and C14) were analysed by means of X-ray diffraction. These samples were chosen because they appeared to

contain a relatively high clay percentage. In addition, the site distribution of these samples (Figure 3.1) provides a satisfactory representation of the sediments in Small Bay

The XRD clay specimens of C7 and C14 were prepared by pipetting clay suspensions (containing approximately 20 mg clay/mL) onto glass slides and allowing them to dry slowly. The clay suspensions of C5, C6 and C7, however, would not adhere to the glass surfaces and so were dried on ceramic discs using a Buchner suction funnel. Both of these drying techniques allow for parallel orientation of the specimens (pers. com., H. Frimmel).

The identification of all the peaks in the diffraction patterns was made according to JCPDS (1980) data. Since XRD is not a very sensitive analytical technique, minerals present in a quantity of less than about five percent of the total clay fraction will not be detected (Whittig and Allardice, 1986). The diffractograms of the five clay samples are fairly similar although peak intensities differ significantly (Figure 3.6).

All five clay samples contain mica, kaolinite and plagioclase feldspars but C4 and C14 also contain quartz, aragonite and calcite. The diffractograms of C7 and C14 indicate the presence of undifferentiated 2:1 layer silicates. The presence of most of these minerals can be explained by the local geology. Chemical and physical processes convert granite into a wide variety of clay minerals by weathering. Water and organisms are responsible for most of the physical weathering of rocks (Allen and Hajek, 1989).

The XRD patterns of muscovite, biotite and illite (mica group minerals) are characterised by the presence of two intense peaks in the region of 10.00 Å and 3.30 Å and a relatively weaker peak at 5.00 Å (Allen and Hajek, 1989). The diffractograms of all five clay samples contain these peaks as well as a relatively large peak at 2.00 Å which may also be attributed to a mica mineral. Micas are 2:1 layered silicates and are non-expanding due to the charge balance between the non-hydrated interlayer cations (typically K^+) and the high layer-charge. Micas are abundant in many rock types, including granites and shales, and in sediments derived from these and other rocks (Allen and Hajek, 1989). Given that illite is a clay mica commonly

found in marine sediments (Libes, 1992) and produces broader peaks than the more crystalline muscovite and biotite minerals, the mica component identified in the clay samples is probably dominated by illite. De la Cruz (1978) identified minor phenocrysts of biotite in granite on the shores of the outer bay, so it is possible that this more crystalline mica mineral may also be present in the sediment clay fraction. Micas serve as precursors for expandable 2:1 minerals such as smectites and vermiculites.

Transformation into these minerals occurs by replacement of the non-exchangeable interlayer cations by hydrated exchangeable cations (Allen and Hajek, 1989). Illites typically have a low cation exchange capacity (10-40 cmoles/kg) (McBride, 1994).

Absolute confirmation of the presence of mica minerals requires further treatment of the XRD samples. Such preparations include glycerol solvation, Mg-saturation, K-saturation and heating to 500 °C. Retention of the 10.00 Å peak following these treatments confirms the presence of micas.

The principal kaolinite peaks are identified at 7.15 Å (100 % intensity) and 3.57 Å (90 %) with a smaller peak at 2.49 Å (70 %). The least intense peak is absent in C5, C6 and C7. Kaolinite is also an abundant marine clay (Libes, 1992). It is a non-expanding 1:1 layer silicate which undergoes little isomorphous substitution and has a low surface area. Consequently, kaolinite has a low cation exchange capacity (1-15 cmoles/kg) (McBride, 1994).

Although accurate quantitative determination of sample components by means of XRD analysis is usually unsuccessful, investigations have shown that the basal peaks of mica and kaolinite have similar relative intensities at similar concentrations (pers. com., H. Frimmel). The basal peaks in Figure 3.6 indicate that these two clay minerals are probably present in similar concentrations in C4, C5, C6 and C7 but that C14 possibly contains more mica than kaolinite.

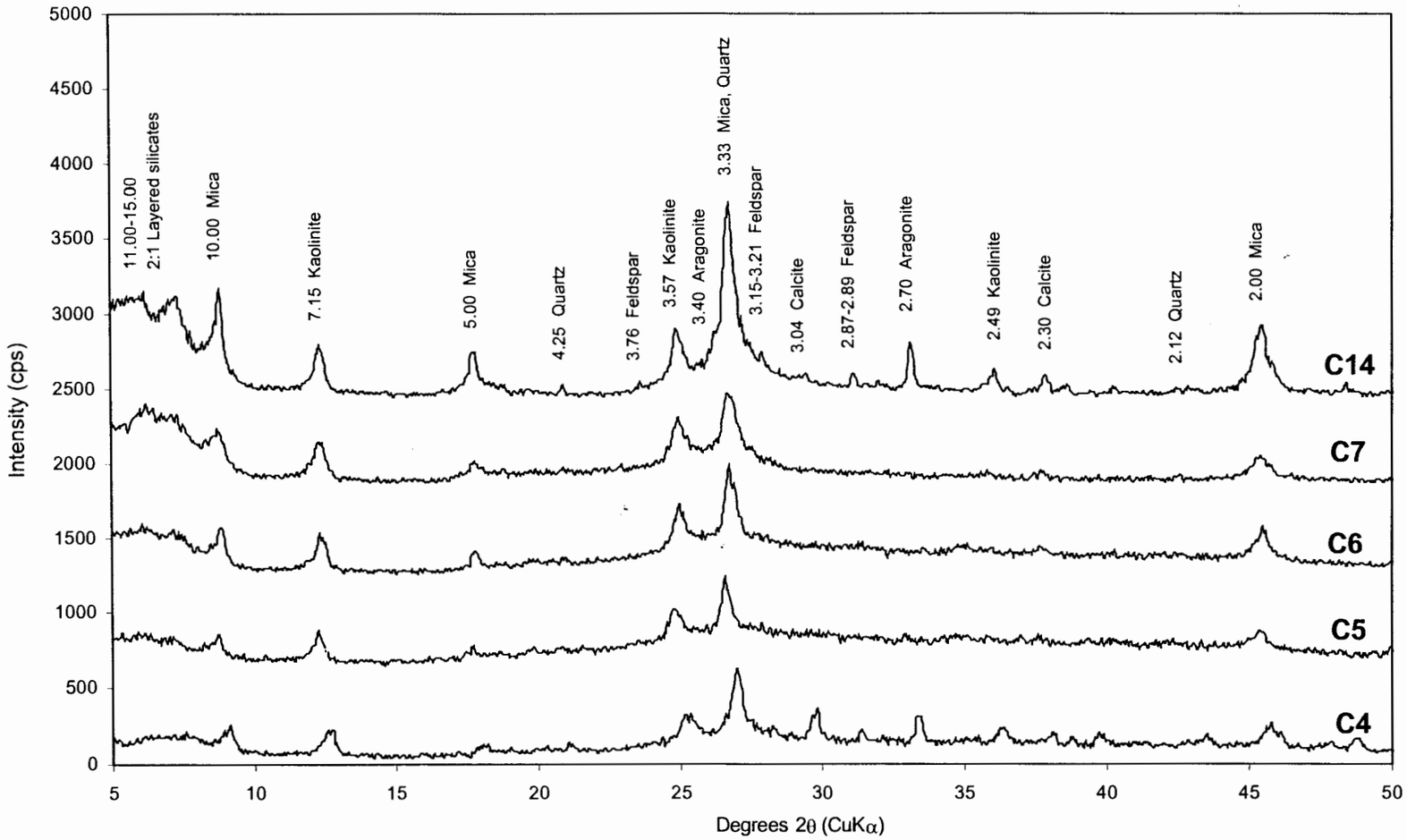


Figure 3.6 X-ray diffraction patterns of the clay fractions of five sediment samples from Small Bay, Saldanha Bay. The d-spacings of identified peaks are given in Å. Patterns are stacked with a constant value of 600 counts per second in between each pattern.

The principal quartz peak occurs at a d-spacing of 3.33 Å and would therefore be hidden by the mica peak at the same position. Since the second strongest quartz peak (at 4.25 Å) is so small in both C4 and C14, yet has a relative intensity of 35 %, it is probable that the peak at 3.33 Å is attributed mainly to the presence of mica. Another minor quartz peak is observed at 2.12 Å in C14. Quartz is one of the most common minerals in the earth's crust and is found in every class of rock (Pough, 1987). Although quartz represents the major component of the sand fraction (0.0625-2.00 mm) and is not usually associated with the clay fraction, the high proportion of SiO_2 (about 49 %) present in the sediments of Small Bay means that it is not surprising that some finely divided quartz has been detected in the clay fractions of C4 and C14.

A series of small peaks between 3.15 and 3.21 Å (20-100 % intensity) on the shoulder of the mica/quartz peak at 3.33 Å, suggests the presence of plagioclase feldspars. The clay diffractogram of C14 also contains a feldspar peak at 3.76 Å (70 % intensity) as well as a series of small peaks between 2.87 and 2.89 Å (10-30 % intensity). Plagioclase feldspars represent a continuous series of mixtures of sodium and calcium aluminium silicates. Examples include albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$) (Pough, 1987). Plagioclase feldspar is an abundant component of granite and is the most important parent mineral for all clay minerals, except montmorillionite (Allen and Hajek, 1989). Ideally, clay samples to be analysed for feldspars should be pretreated to remove carbonates, organic matter and iron oxides (Allen and Hajek, 1989).

Calcite is identified in C4 and C14 by the presence of a peak at 3.04 Å (100 % intensity) and a smaller peak at 2.30 Å. The principle calcite peak in C14, however, is less intense than the peak at 2.30 Å in the same X-ray pattern. Calcite deposits in marine sediments are usually the result of aragonite transformation (Berner, 1975).

In C4 and C14 the principal aragonite peak at 3.40 Å is partially hidden, situated in between the kaolinite peak at 3.57 Å and the mica/quartz peak at 3.33 Å. A less intense aragonite peak (50 % intensity) at 2.70 Å is also observed in the X-ray patterns of C4 and C14. Aragonite is far rarer that calcite, usually being deposited from warmer solutions than the latter. One of the sources of aragonite in the Small Bay sediments may be the mussel populations, since molluscs secrete aragonite to form the inner surfaces of their shells (Pough, 1987).

A series of overlapping peaks is seen in the diffractograms of C7 and C14, between 11 and 15 Å (about 6-8 °2θ). These peaks suggest the presence of undifferentiated 2:1 layer silicates such as chlorite, smectite and vermiculite. Further treatment of the XRD samples would be required to make positive identifications of these minerals. Chlorite is a non-swelling clay with a low cation exchange capacity of 5-30 cmoles/kg (Libes, 1992). Smectites and vermiculites however, are expanding clays that can undergo isomorphous substitution. Aluminium can substitute for Si in the tetrahedral sheets and Mg, Fe, Cr, Zn, Li often substitute for Al or Mg in the octahedral sheets. Typically, smectites and vermiculites have fairly high cation exchange capacities of 70-120 and 100-150 cmoles/kg respectively (McBride, 1994). Compared with the kaolinite, therefore, this component is likely to exert a significant effect on metal mobility in the sediments.

3.4.6 Elemental composition

The major element composition of marine sediments is largely controlled by the relative proportions of the sediment-forming minerals. The principal minerals are the clays, carbonates and opal or quartz. Aluminium is largely concentrated in the clays, calcium in the carbonates and silicon in the resistate fraction (Chester, 1990). Iron and manganese are usually present as oxyhydroxides in oxic sediments and as metal sulfides in strongly anoxic sediments. Potassium tends to be associated with the clay fraction, in the form of clay minerals such as illite.

Major element analyses can, therefore, be used to quantitatively assess the distributions of the dominant minerals in a sediment system. The SiO_2 content generally reflects the distribution of the quartz or sand fraction, CaO and MgO the carbonate mineral fraction, and Al_2O_3 the mud or clay fraction. Since Fe and Mn are considered to be the principal scavenging agents for many trace metals, their concentrations reflect the distribution of metal adsorption phases. Aluminium oxyhydroxides have also been noted as playing a role in the uptake of trace metals but the majority of Al will be present in association with the clay minerals.

Concentrations of major elements and a comprehensive selection of trace elements in the sediments were determined by means of WDXRFS. The results of these analyses are presented in Tables 3.5 and 3.6 respectively. Cadmium is not included in Table 3.6 as it is present in the sediments in concentrations which are below the lower limit of Cd detection

for WDXRFS (4 ppm). The major and trace element data provide the basis for a geochemical investigation of the sediment solid phase. In addition, the concentrations of selected metals were determined by extracting them in an acid digest that was analysed by FAAS (Table 3.7). The objective of performing this second set of analyses was to extract the readily available trace metals from the solid phase. The partition coefficients of Cd, Cu, Pb and Zn were calculated using the acid digest concentrations of these metals. These coefficients are discussed in chapter 5.

In order to investigate the relationships between different elements a Spearman rank order correlation matrix was performed with selected variables using STATISTICA software. The results of this are given in Table 3.8. Shaded coefficients are significant at $p<0.01$ (n=13 for all correlations). The concentrations of Cu, Pb and Zn used in the statistical analyses were those determined by WDXRFS.

3.4.6.1 Element determination by WDXRFS

The results of the major element analyses on the sediment samples in Table 3.5 reveal that for all samples, the summation of the major elements is close to 100 % (totals range from 97.2 to 101.4 %). This indicates that the major element data are reliable.

Although silica occurs in both quartz and clay minerals it is usually a good indication of the relative proportion of sand present in sediments. The concentrations of SiO_2 in the sediments vary greatly, ranging from 14.71 (C4) to 85.17 % (C3). The average SiO_2 content is approximately 49 %, which is similar to the average concentration of 57 % detected in 1977 by Willis *et al.* (1977). These authors also reported a large concentration range for silica. Strong, negative correlations exist between silica and CaO as well as between silica and MgO. Since CaO and MgO represent the carbonate fraction, this is to be expected. The trace metal Sr is also negatively correlated with SiO_2 and this is likely to be due to the ability of Sr to substitute for Ca in $CaCO_3$ minerals (Wehmiller, 1972). (The Spearman R for the correlation between CaO and Sr is 0.90).

Table 3.5 Results of the WDXRFS major element analyses. Concentrations are expressed in mass percent of the relevant oxides.

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	H_2O	LOI	TOTAL
C1	25.60	0.16	2.64	1.47	0.01	0.85	33.83	0.85	0.64	0.94	1.37	1.12	31.4	100.9
C2	83.93	0.17	5.02	1.07	0.01	0.30	3.01	0.61	2.17	0.28	0.03	0.35	3.57	100.5
C3	85.17	0.17	4.14	1.07	0.01	0.33	3.48	0.52	1.88	0.56	0.05	0.42	3.59	101.4
C4	14.71	0.08	1.87	0.85	0.00	1.86	39.66	0.29	0.38	0.40	0.53	1.01	35.5	97.2
C5	29.62	0.15	2.48	1.32	0.01	0.62	32.60	0.81	0.84	0.30	1.03	0.71	29.5	100.0
C6	33.46	0.17	3.36	1.33	0.01	1.36	29.11	0.76	0.82	0.41	0.73	1.35	27.4	100.3
C7	31.93	0.16	3.39	1.55	0.01	1.28	28.34	0.68	0.74	0.40	0.87	1.66	28.7	99.7
C8	53.89	0.10	1.60	0.56	0.00	0.67	22.81	0.48	0.65	0.44	0.31	0.40	19.1	101.0
C9	49.38	0.08	1.42	0.46	0.00	0.64	25.10	0.51	0.61	0.47	0.36	0.38	20.8	100.2
C11	69.63	0.08	1.90	0.61	0.00	0.39	14.25	0.48	0.90	0.36	0.15	0.27	11.6	100.6
C12	53.37	0.11	2.31	0.68	0.01	0.58	21.76	0.61	0.90	0.49	0.29	0.52	18.0	99.6
C13	53.90	0.12	2.31	0.63	0.01	0.57	21.88	0.56	0.92	0.46	0.28	0.48	17.8	99.9
C14	49.14	0.22	4.53	1.57	0.01	1.30	19.24	0.76	1.26	0.46	0.85	1.12	19.3	99.7

Table 3.6 Results of all trace element analyses by WDXRFS. Concentrations are given in mg/kg.

Sample	Mo	Nb	Zr	Y	Sr	U	Rb	Th	Pb	Cu	Zn	Ni	Co	Mn	Cr	V	S
C1	4.1	2.8	77	6.8	1043	5.4	30	5.7	77	43	222	12	2.1	60	55	26	10141
C2	3.0	5.7	138	11	134	<2.2	87	3.8	18	12	30	9.6	2.1	89	41	16	2726
C3	3.7	6.0	145	10	149	2.5	68	3.1	17	12	41	11	1.9	90	43	14	2196
C4	<1.3	2.8	40	12	1415	3.6	23	<3.8	13	8.1	24	5.7	1.5	45	31	17	2887
C5	9.9	3.5	45	7.2	894	3.2	33	<3.6	287	143	279	13	5.7	62	50	17	7498
C6	3.6	3.4	73	12	1031	<2.8	36	<3.5	9.3	11	55	12	2.3	68	47	26	5964
C7	10	3.3	53	12	944	3.0	36	5.0	13	13	78	15	2.2	74	57	33	7294
C8	1.6	2.6	116	14	968	<2.6	23	<3.3	<4.6	5.8	14	5.0	<1.3	42	25	9.0	3418
C9	<1.2	2.4	74	11	1097	<2.7	22	<3.4	7.0	4.9	10	4.7	<1.3	34	24	7.2	3206
C11	<1.1	1.4	51	10	459	<2.4	30	<3.1	19	5.8	10	5.2	1.7	43	28	10	2000
C12	1.3	2.5	63	13	757	<2.6	32	<3.3	22	9.2	18	5.5	<1.3	38	31	14	3270
C13	<1.1	1.7	82	13	785	<2.6	32	<3.3	26	11	21	4.7	<1.3	40	30	12	3537
C14	4.1	4.7	105	16	675	3.4	53	4.8	27	33	90	14	3.1	78	59	30	8816

Table 3.7 Concentrations (mg/kg) of metals extracted using nitric acid / perchloric acid / hydrogen peroxide.

Sample	Al	Mn	Fe	Na	K	Mg	Ca	Cd	Cu	Pb	Zn
C1	9241	32	11692	2958	964	4667	320000	2.31	36	100	211
C2	5867	41	6857	320	836	1304	30698	0.71	10	16	21
C3	5440	42	6857	340	1654	1304	37674	0.79	11	16	28
C4	8414	25	6857	2028	1234	10184	493023	1.07	6.4	42	17
C5	6080	33	9231	2563	836	3267	384000	1.93	137	256	272
C6	13379	36	10154	2732	2075	7421	344000	1.57	9.1	40	39
C7	15034	39	12615	3099	2260	6789	344000	2.25	12	40	58
C8	3221	20	3726	1653	500	3141	269231	0.76	4.7	29	6.7
C9	2800	21	3375	2169	621	3333	336000	0.57	4.9	30	4.4
C11	2692	25	4258	498	500	1505	184615	0.55	6.2	29	4.6
C12	5641	21	4945	1628	845	2759	323077	0.55	9.0	43	12
C13	4769	22	4258	1604	639	2822	292308	0.76	10	43	14
C14	14999	38	11726	1694	2410	6113	238846	2.15	29	43	67

Silica is positively correlated with K_2O and this may be due to the fact that potassium is held in the interlayer spaces of some layered silicates, of which illite is a prime example. Silica is negatively correlated with SO_3, LOI and POC at the 99 % confidence level. These relationships may be explained by the tendency of organic matter and sulfides to be associated with one another in the finer mud fraction.

The percentages of SiO_2, CaO, Al_2O_3, Fe_2O_3 as well as the LOI component are presented in Figure 3.7. LOI represents the fraction of the sediment that is lost during the roasting process in the preparation of the fusion discs for analysis by XRF spectrometry. It includes structural water, organic matter, CO_2 from carbonate minerals and SO_2 from sulfide minerals.

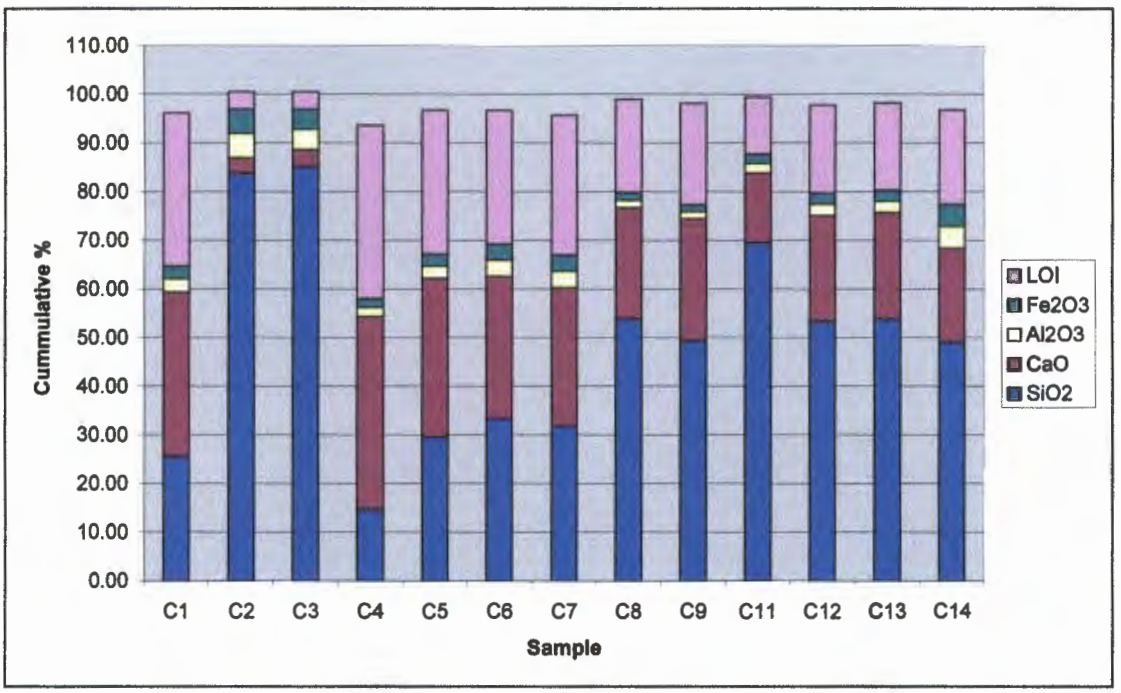


Figure 3.7 The major element composition of the Small Bay sediment samples.

An average CaO concentration of 23 % has been calculated for the range 3.01 % (C2) to 39.66 % (C4). Willis *et al.* (1977) reported a very similar concentration of about 21 % for the Saldanha Bay sediments.

It is not surprising that the significant correlations of CaO are the inverse of those for SiO_2. Calcium oxide is positively correlated with MgO, SO_3, LOI, POC and Sr, and negatively correlated with K_2O.

Given that the average Al_2O_3 content is only 2.84 %, it can be said that the sediments in Small Bay have a low clay mineral content. The amount of Al_2O_3 ranges from 1.42 % (C9) to 5.02 % (C2). Willis *et al.* (1977) found that the sediments contained almost no clay minerals and reported an Al_2O_3 content of 2.02 %. Since then, sections of Small Bay have been dredged to create channels for ships and to allow for the building and subsequent extension of the ore jetty. It is possible that the removal of sediment from certain areas may have exposed underlying weathered material. The occurrence of relatively high Al_2O_3 concentrations in C14 (collected near the ore jetty), and in C2 and C3 (both in the fishing harbour), may be related to dredging activities.

Three major elements are strongly correlated with Al_2O_3: they are TiO_2, MnO and Fe_2O_3. It is suggested that, although clay minerals are present in relatively small concentrations in the sediments, the 2:1 layer silicates detected in the clay fractions of the sediments are involved in the adsorption of many trace metals. Strong, positive correlations exist between Al_2O_3 and Nb, Rb, Cu, Ni, Co, Cr and V.

A small range of Fe_2O_3 exists in the sediments: 0.46 % (C9) to 1.57 % (C14). The average Fe_2O_3 concentration of 1.01 % is somewhat higher than the 0.36 % reported by Willis *et al.* (1977). The Fe_2O_3 component of the sediments is positively correlated with MnO, Al_2O_3 and TiO_2. Given that the sediments are fairly anoxic, it is likely that most of the iron is present in the form of iron sulfides or $FeCO_3$ (siderite).

Due to the typical metal-scavenging behaviour of Fe-sulfides in sediments, it is not surprising to find correlations existing between Fe_2O_3 and Cu, Zn, Ni, Co, Cr and V. The strongest relationship involving Fe_2O_3 and a trace metal is that of Cr. In general, Cr(III) species are strongly adsorbed on oxides and clays but it also readily substitutes for Fe^{3+} in minerals (McBride, 1994).

Table 3.8 Spearman rank order correlation matrix for major and trace elements in the sediments of Small Bay. Shaded correlation coefficients are significant at p<0.01 (n=13 for all correlations except POC, where n=12).

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	LOI	POC
SiO_2	1.00	0.14	0.15	-0.44	0.16	-0.82	-0.92	-0.38	0.73	0.02	-0.90	-0.98	-0.86
TiO_2	0.14	1.00	0.94	0.75	0.92	-0.06	-0.33	0.66	0.60	0.08	0.08	-0.21	-0.21
Al_2O_3	0.15	0.94	1.00	0.80	0.93	-0.13	-0.37	0.61	0.67	-0.07	0.01	-0.24	-0.16
Fe_2O_3	-0.44	0.75	0.80	1.00	0.71	0.40	0.19	0.78	0.18	-0.00	0.58	0.36	0.41
MnO	0.16	0.92	0.93	0.71	1.00	-0.24	-0.33	0.64	0.66	0.02	0.03	-0.22	-0.19
MgO	-0.82	-0.06	-0.13	0.40	-0.24	1.00	0.74	0.17	-0.67	0.07	0.75	0.82	0.68
CaO	-0.92	-0.33	-0.37	0.19	-0.33	0.74	1.00	0.22	-0.85	0.01	0.80	0.96	0.77
Na_2O	-0.38	0.66	0.61	0.78	0.64	0.17	0.22	1.00	0.16	0.12	0.62	0.31	0.28
K_2O	0.73	0.60	0.67	0.18	0.66	-0.67	-0.85	0.16	1.00	-0.12	-0.58	-0.80	-0.74
P_2O_5	0.02	0.08	-0.07	-0.00	0.02	0.07	0.01	0.12	-0.12	1.00	0.10	0.02	-0.27
SO_3	-0.90	0.08	0.01	0.58	0.03	0.75	0.80	0.62	-0.58	0.10	1.00	0.90	0.73
LOI	-0.98	-0.21	-0.24	0.36	-0.22	0.82	0.95	0.31	-0.80	0.02	0.90	1.00	0.86
POC	-0.86	-0.21	-0.16	0.41	-0.19	0.68	0.78	0.28	-0.74	-0.27	0.73	0.86	1.00
Mo	-0.16	-0.43	-0.34	-0.18	-0.37	0.04	0.21	-0.25	-0.20	-0.18	0.10	0.20	0.31
Nb	-0.01	0.82	0.81	0.68	0.88	0.03	-0.15	0.44	0.40	-0.10	0.10	-0.02	0.02
Zr	0.64	0.57	0.41	-0.00	0.46	-0.40	-0.61	0.03	0.52	0.39	-0.44	-0.62	-0.69
Y	0.08	0.04	-0.08	-0.08	-0.22	0.33	-0.16	-0.21	0.07	0.08	-0.10	-0.12	-0.40
Sr	-0.76	-0.47	-0.58	-0.09	-0.56	0.74	0.90	-0.05	-0.96	0.17	0.62	0.84	0.69
U	0.30	-0.61	-0.65	-0.76	-0.72	-0.21	-0.16	-0.42	-0.15	0.00	-0.37	-0.29	-0.29
Rb	0.32	0.89	0.95	0.65	0.91	-0.28	-0.50	0.49	0.79	-0.17	-0.17	-0.40	-0.37
Th	0.04	-0.79	-0.84	-0.73	-0.84	-0.03	0.14	-0.39	-0.37	-0.03	-0.09	0.00	-0.06
Pb	-0.03	0.06	0.03	0.10	0.14	-0.16	-0.01	0.32	0.19	0.04	0.21	-0.00	-0.06
Cu	-0.32	0.72	0.76	0.88	0.81	0.07	0.13	0.84	0.31	0.01	0.51	0.25	0.27
Zn	-0.52	0.68	0.67	0.91	0.73	0.33	0.36	0.84	0.08	0.01	0.67	0.47	0.47
Cd	-0.67	0.49	0.45	0.84	0.44	0.61	0.55	0.65	-0.22	0.09	0.80	0.66	0.62
Ni	-0.44	0.68	0.74	0.95	0.69	0.38	0.20	0.71	0.15	-0.15	0.58	0.37	0.48
Co	-0.32	0.67	0.72	0.85	0.69	0.25	0.10	0.69	0.26	-0.37	0.48	0.25	0.46
Mn	0.08	0.82	0.89	0.74	0.86	-0.03	-0.25	0.39	0.51	-0.21	0.03	-0.12	0.07
Cr	-0.45	0.73	0.78	0.99	0.73	0.37	0.20	0.78	0.18	0.01	0.60	0.37	0.42
V	-0.57	0.64	0.70	0.97	0.58	0.53	0.33	0.71	0.04	-0.12	0.63	0.48	0.55
S	-0.65	0.37	0.23	0.64	0.24	0.55	0.53	0.79	-0.24	0.21	0.86	0.61	0.41

Table 3.8 continued

	Mo	Nb	Zr	Y	Sr	U	Rb	Th	Pb	Cu	Zn	Cd	Ni	Co	Mn	Cr	V	S
Mo	1.00	-0.47	-0.44	-0.23	0.21	0.15	-0.36	0.33	-0.20	-0.13	-0.16	0.02	-0.21	-0.19	-0.26	-0.16	-0.12	-0.08
Nb	-0.47	1.00	0.37	-0.14	-0.32	-0.82	0.79	-0.90	0.00	0.67	0.70	0.50	0.72	0.73	0.91	0.69	0.61	0.16
Zr	-0.44	0.37	1.00	0.18	-0.45	-0.07	0.41	-0.40	0.13	0.06	-0.01	-0.06	-0.12	-0.08	0.34	-0.02	-0.18	-0.08
Y	-0.23	-0.14	0.18	1.00	0.00	0.17	-0.00	0.12	0.03	-0.32	-0.25	-0.12	-0.12	-0.21	-0.20	-0.11	-0.02	0.13
Sr	0.21	-0.32	-0.45	0.00	1.00	0.10	-0.70	0.31	-0..22	-0.23	0.03	0.32	-0.11	-0.21	-0.46	-0.10	0.05	0.35
U	0.15	-0.82	-0.07	0.17	0.10	1.00	-0.59	0.87	-0.06	-0.77	-0.81	-0.74	-0.80	-0.66	-0.78	-0.80	-0.73	-0.33
Rb	-0.36	0.79	0.41	-0.00	-0.70	-0.59	1.00	-0.74	-0.01	0.64	0.54	0.26	0.64	0.65-	0.85	0.64	0.56	0.07
Th	0.33	-0.90	-0.40	0.12	0.31	0.87	-0.74	1.00	0.00	-0.70	-0.70	-0.58	-0.69	-0.59	-0.89	-0.74	-0.66	-0.18
Pb	-0.20	0.00	0.13	0.03	-0.22	-0.06	-0.01	0.00	1.00	0.39	0.29	0.19	0.09	0.20	-0.04	0.16	-0.00	0.44
Cu	-0.13	0.67	0.06	-0.32	-0.23	-0.77	0.64	-0.70	0.39	1.00	0.95	0.77	0.85	0.80	0.68	0.91	0.79	0.63
Zn	-0.16	0.70	-0.01	-0.25	0.03	-0.81	0.54	-0.70	0.29	0.95	1.00	0.88	0.88	0.82	0.65	0.93	0.86	0.73
Cd	0.02	0.50	-0.06	-0.12	0.32	-0.74	0.26	-0.58	0.19	0.77	0.88	1.00	0.79	0.67	0.52	0.85	0.84	0.78
Ni	-0.21	0.72	-0.12	-0.12	-0.11	-0.80	0.64	-0.69	0.09	0.85	0.88	0.79	1.00	0.92	0.76	0.96	0.95	0.56
Co	-0.19	0.73	-0.08	-0.21	-0.21	-0.66	0.65	-0.59	0.20	0.80	0.82	0.67	0.92	1.00	0.78	0.85	0.82	0.48
Mn	-0.26	0.91	0.34	-0.20	-0.46	-0.78	0.85	-0.89	-0.04	0.68	0.65	0.52	0.76	0.78	1.00	0.74	0.67	0.08
Cr	-0.16	0.69	-0.02	-0.11	-0.10	-0.80	0.64	-0.74	0.16	0.91	0.93	0.85	0.96	0.85	0.74	1.00	0.96	0.65
V	-0.12	0.61	-0.18	-0.02	0.05	-0.73	0.56	-0.66	-0.00	0.79	0.86	0.84	0.95	0.82	0.67	0.96	1.00	0.63
S	-0.08	0.16	-0.08	0.13	0.35	-0.33	0.07	-0.18	0.44	0.63	0.73	0.78	0.56	0.48	0.08	0.65	0.63	1.00

The LOI component in the sediments ranges from 3.57 % (C2) to 35.5 % (C4) with an average of 20.5%. It is not unexpected to discover strong correlations existing between LOI and the components, CaO, MgO, SO_3, S and POC. The material lost from the sediments in the oven (1000 °C) during the preparation of the XRF fusion discs was obviously of organic, carbonate and sulphidic origin.

The correlations between potassium and silica at the 99 % confidence level and potassium and Al_2O_3 at the 95 % confidence level indicate that a significant proportion of K in the sediments exists as adsorbed K^+ ions in the inter-layer regions of clay minerals (likely to be illite).

The concentrations of Cd in the sediments (Table 3.7) range from 0.55 mg/kg (C11 and C12) to 2.31 mg/kg (C1) and the average Cd level is 1.23 mg/kg. Cadmium in the Saldanha Bay sediments was not determined in 1977 by Willis *et al.* (1977). A more recent concentration of 0.4 mg Cd/kg was obtained by Gardner *et al.* (1985) in 1983. The current average Cd concentration in the sediments is approximately 3 times this level.

Cadmium is very strongly correlated with Fe_2O_3, S and SO_3 at the 99 % confidence level. At a lower confidence level (95 %), positive correlations also exist between Cd and POC, MgO, CaO, Na_2O and LOI. These results suggest that Cd is largely associated with Fe-sulfides, and to a lesser extent with organic material and carbonates.

The highest concentrations of Cu, Pb and Zn were all detected in sample C5 and the lowest in either C8 or C9. Copper concentrations range from about 5 (C9) to 143 mg/kg (C5). The average Cu concentration of 24 mg/kg drops to 14 mg/kg if the exceptionally high concentration of C5 is excluded, and drops further to 9.3 mg/kg if the outlier values of C1 and C14 are excluded. The latter average Cu concentration (9.3 mg/kg; n=10) is at least 10 times higher than the average level detected by Willis *et al.* (1977) (<1 mg/kg) and roughly 2.5 times the concentration reported by Gardner *et al.* (1985) for the year 1983 (3.8 mg/kg). Copper is positively correlated with TiO_2, Al_2O_3, Fe_2O_3, MnO and Na_2O at the 99 % confidence level, and with S at $p<0.05$. No correlation exists for POC. It can

be inferred that most of the Cu in the sediments is associated with clay minerals and Fe and Mn sulfides. The statistics indicate however, that copper is associated with a host of other trace metals including, Cd, Zn, Ni, Co, Cr and V ($p<0.01$).

Lead concentrations range from less than 4.6 mg/kg (C8) to 287 mg/kg (C5). The average lead concentration is 41 mg/kg. When the outlier concentration of C5 is excluded the average drops to about 20 mg/kg, which is about 3.5 times greater than the concentration determined by Gardner *et al.* (1985) in 1983 (5.8 mg/kg). The results of the statistical analysis suggest that lead is uncorrelated (at $p<0.05$) with other sediment components. This is unexpected, as lead tends to associate strongly with certain sediment components including organic material and sulfides. It also exists in the form of Pb-carbonate and Pb-phosphate.

The range of Zn in the sediments is 10 (C9 and C11) to 279 mg/kg (C5). An average concentration of approximately 69 mg/kg was calculated for the 13 samples but this is reduced to approximately 36 mg/kg on exclusion of the exceptionally high concentrations in C1 and C5. The average concentration of 36 mg/kg is more than five times greater than that determined by Willis *et al.* (1977) (7 mg/kg) and about 2.5 times that found in 1983 (15 mg/kg) by Gardner *et al.* (1985). The statistical analyses suggest that the associations of Zn in the sediment solid phase are very similar to those of Cu. Zinc is most strongly correlated with Fe_2O_3 and Cu at the 99 % confidence level. It is probable that Zn is largely associated with Fe and Mn sulfides and clay minerals. The trace metals Cd, Ni, Co, Cr and V are also correlated with zinc.

The reason for enormously high concentrations of Cu, Pb and Zn in sample C5 (Tables 3.6 and 3.7) is unknown. This sample, which was collected from the fish factory region of Small Bay, also yielded very high concentrations of AVS and SEM (Table 3.2). At this point, it is suggested that the elevated levels of Cu, Pb and Zn in this dark and muddy sediment sample are related to its high sulfide content. However, since this corner of the bay is relatively sheltered and still, it is possible that metal debris from the harbour and the boats is collecting in the undisturbed sediment.

3.4.6.2 Metal concentrations in acid digest

An acid digest was performed to extract the readily available trace metals from the sediment solid phase. A mixture of concentrated nitric acid, perchloric acid and hydrogen peroxide was used to extract metals from sub-samples of the oven-dried (but not roasted) material that was used to prepare the discs and briquettes for WDXRFS. The acid digest was analysed for a selection of metals by means of FAAS (Table 3.7).

According to Janssen *et al.* (1996) concentrated nitric acid will partly dissolve mineral lattices, and Luoma and Bryan (1981) report that nearly 100 % of the trace metal content of sediments can be released by using HNO_3 (concentrated), compared to a total sample dissolution by hydrogen fluoride.

Spearman rank correlations were used to assess the agreement between the data obtained by WDXRFS and FAAS. These results are given in Table 3.9. Although consensus is desired for all the sediment constituents shown in Table 3.9, the correlations for Cu, Pb and Zn are of most importance. Very strong correlations exist between the respective Cu and Zn data sets. This is not the case however for Pb. Given that the lead concentrations detected by FAAS were generally higher than those determined by WDXRFS, it is possible that the acids or laboratory equipment used in the acid digest may have been contaminated with lead. Anthropogenic sources of lead are ubiquitous in urban environments (vehicle exhausts, etc.).

Agreement between the two sets of data is also observed for Al, Mn, Fe, Mg and Ca. The very strong correlations for Mn, Fe, Mg and Ca at the 95 % confidence level may be due to the complete extraction of these components by the acid digestion. The correlation for Al is slightly poorer in comparison. The majority of the Al concentrations determined by FAAS are lower than the corresponding WDXRFS values. Since Al is mainly associated with the clay fraction, this supports the assertion that the acid digestion does not break down the crystalline silicates entirely.

Table 3.9 Results of Spearman rank order correlations for sediment metals detected by WDXRFS versus FAAS (n=13).

WDXRFS *(Tables 3.5 and 3.6)* vs FAAS *(Table 3.7)*	Spearman *R*	Correlation significant at *P*<0.05
Cu vs Cu	0.99	✔
Pb vs Pb	0.48	✘
Zn vs Zn	0.99	✔
Al_2O_3 vs Al	0.61	✔
MnO vs Mn	0.87	✔
Fe_2O_3 vs Fe	0.99	✔
Na_2O vs Na	0.50	✘
K_2O vs K	0.09	✘
MgO vs Mg	0.97	✔
CaO vs Ca	0.88	✔

Cadmium omitted as it was not detected by WDXRFS.

The partial extraction may also be responsible for the extremely weak correlation between the WDXRFS determined K and the K detected by FAAS. Potassium concentrations in the acid digest are consistently lower than those determined by WDXRFS and this may be due to K not being displaced from clay minerals such as illite. The high density of surface charge on illites reduces the interlayer space so that H_2O and other large cations cannot enter. Due to the strong charges however, relatively small cations such as K^+ are adsorbed but not readily exchanged (Dixon and Weed, 1989). Likewise, the poor correlation between the two sodium data sets may be attributed to sodium ions trapped in the interlayer spaces of clay minerals that are resistant to acid attack. The levels of Na in the acid digest are generally lower than those detected by WDXRFS.

3.5 Conclusions

The sediments of Small Bay in Saldanha Bay are highly variable with respect to sulfide content, organic matter content, major element concentrations as well as trace metal concentrations.

The sulfide concentration of a particular sediment probably depends on a number of factors, such as the quantity and quality of organic matter entering the sediment system at that site, the rate of decomposition of the organic material by bacteria and other organisms, and the extent to which the sediment is disturbed by water currents or marine life. The fact that the highest concentrations of simultaneously extracted Cu, Cd, Pb and Zn were all obtained from highly reduced sediment samples, suggests that sulfides play an important role in the scavenging of these metals. There are significant correlations between AVS and SEM-Pb ($p<0.01$) and AVS and SEM-Fe ($p<0.05$).

Ratios of AVS to SEM cannot be used to make accurate evaluations of the risks that the Small Bay sediments may pose towards aquatic life, since, it is necessary to account for a much broader spectrum of potentially toxic trace metals. There are also a number of limitations associated with the HCl extraction of sulfidic components.

Generally, the sediment samples which are dark in colour and muddy, have higher organic carbon concentrations than the samples consisting almost entirely of light-coloured sand. The broad range of C/N ratios (0.62 to 35) may be due to varying degrees of both bioturbation and resuspension of organic material in the bay.

Given the anoxic nature of the sediments, it is doubtful whether the concentrations of Fe and Mn in the hydroxylamine hydrochloride/HCl extraction provide a true reflection of the quantities of reducible iron and manganese in the sediments. Most of the Fe and Mn in these digestions is likely to have been associated with sulfides.

The clay mineralogy of the sediments in Small Bay can largely be explained by the geology of the region. Granite is weathered by chemical and physical processes to form a wide range of clay minerals. Mica (probably illite), kaolinite, quartz, plagioclase feldspars, aragonite, calcite and undifferentiated 2: 1 layer silicates have been found in some or all of the clay fractions (in concentrations of no less than 5 % of the clay fraction). Of these components, the 2:1 layer silicates would be the minerals most likely to contribute to the cation exchange capacity of the sediment solid phase.

Not surprisingly, the major element composition of the sediments has barely changed over the past two decades. The sediments are composed mainly of SiO_2 and $CaCO_3$.

Average concentrations of Cd, Cu, Pb and Zn have all increased slightly over the past 15 years. Very high trace metal concentrations have been detected but these are localised within the bay.

Statistical analyses suggest that Cd is largely associated with Fe-sulfides and to a lesser extent, with organic material and carbonates. Copper appears to be associated with clay minerals and sulfides. The behaviour of Cu is very similar to that of Zn: both metals are probably associated with clay minerals and iron and manganese sulfides. Surprisingly, lead is uncorrelated with any of the solid phase parameters at the 95 % confidence level.

CHAPTER 4

Geochemistry of the sediment aqueous phase

4.1 Introduction

Sediments in natural systems are formed by the sedimentation of particles from the overlying water column. During this process water is trapped in the sediment, forming the interstitial or pore water. Chemical species that were present in the water column and adsorbed to the suspended sediment will also be trapped in the bottom sediment during sedimentation (Bufflap *et al.*, 1995). Consequently, sediments can act as sinks for pollutants by removing them from the water column. Within the sediment system chemical species tend toward equilibrium between the solid and aqueous phases. Due to diagenetic and geochemical processes such as precipitation, adsorption, sulfide formation, remineralisation, dissolution and uptake by living organisms, the concentrations of a chemical species in these phases will not be the same. Knowledge of sediment pore water concentrations is required to evaluate the partitioning of chemical species between the solid and aqueous phases. It is also useful in assessing the contribution which the sediments make toward the pollution of the overlying water, since bioavailability and toxicity of heavy metals in sediments can be expressed in terms of pore water concentrations (Janssen *et al.*, 1996).

The objective of this chapter is therefore to characterise the aqueous geochemistry of the sediment system in terms of major constituents and trace metal concentrations. The chapter includes a description of the sampling procedures and the analytical techniques that were used. A large part of this chapter focuses on a geochemical interpretation of the analytical results.

4.2 Sampling

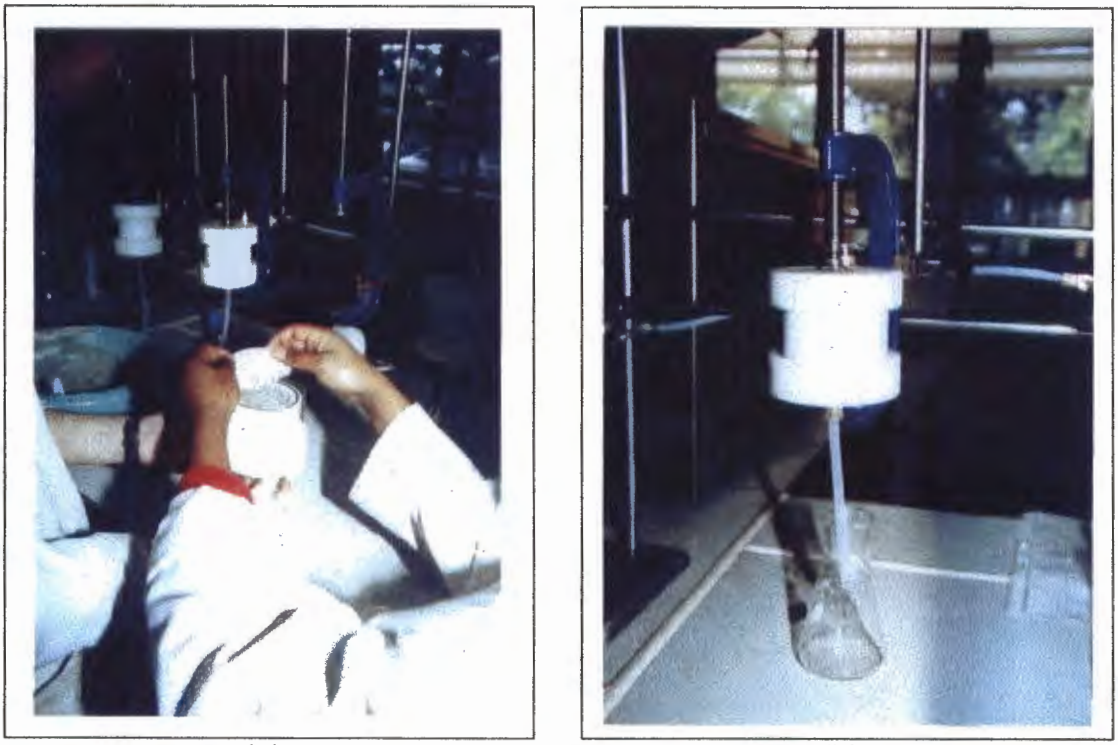
Sediment cores were collected during August (3-7) 1998. Details of the sampling protocol are described in section 3.2 and the removal of the interstitial water from the sediments is described in the next section. The pore water samples obtained from the

sediments are named PW1 to PW9 and PW11 to PW14. The locations of the sampling sites are shown in Figure 3.1.

4.3 Sample handling and preparation

The handling and preparation of the sediment samples prior to the squeezing process are discussed in section 3.2.3.

Five gas-operated squeezers were used to extract the interstitial water from the sediment samples. The Teflon® squeezers (Reeburgh, 1967), shown in Figures 4.1(a) and 4.1(b), use gas pressure (either argon or nitrogen) to act against a latex diaphragm and compress the sediment, forcing the interstitial water through filters into a conical flask.



(a) (b)

Figure 4.1 Teflon® squeezers used to remove pore water from the sediment samples. The photograph in (a) shows placement of the latex membrane on top of the packed sediment. The photograph in (b) shows interstitial water being collected from a tightly clamped squeezer.

Care was taken to remove large shells from the sediment prior to squeezing, to prevent tearing of the diaphragm. The interstitial water was forced through a nylon disc filter and a disc of rough filter paper. Gas pressure was increased gradually up to 500 kPa over a period of 5 to 10 minutes. Each squeezer contained approximately 140 mL of sediment. The squeezing process took between one and two hours, depending on the length of the core. On average, squeezing removed 25 % of the interstitial water, which was collected in conical flasks to be transferred to plastic bottles for storage. pH measurements were taken on the composite water samples at room temperature. The bottles used for storing the pore waters had been acid washed, followed by thorough rinsing in deionised water. Efforts were made to minimise the exposure of the pore water samples to the atmosphere before pH measurements were taken.

Teflon® is recommended as a material suitable for trace metal analysis as it is easily cleaned of metals (Luther, 1995).

4.4 Analytical methods

Summaries of the analytical procedures used to characterise the sediment pore water are presented in this section. All samples were filtered through a 0.45 μm filter prior to analysis to remove suspended particulate matter, although pH measurements were taken both before and after filtration. All chemical analyses except electrical conductivity (EC) and alkalinity were performed at the CSIR in Stellenbosch. EC and alkalinity determinations were done in the Department of Geological Sciences, University of Cape Town.

To ensure the accuracy and precision of some of the analyses, certain samples were analysed in duplicate and standards were used in most cases. The details of these procedures and the quality control data are presented in Appendix D.

4.4.1 pH

The pH was measured using a Radiometer 29 pH meter at room temperature. The meter determines hydrogen ion activity electrometrically using a combined glass indicator-reference electrode. Calibration of the instrument was performed using pH 4 and pH 7 buffer solutions. The method used corresponds with the conventional procedure for freshwater pH analysis. However, according to the recommendations of IUPAC, a slightly different approach should be taken when measuring pH in seawater. It is important for example, to match the buffer solutions to the ionic strength of the samples (Bates, 1982; Covington and Whitfield, 1988). The fact that the preferable method of pH determination was not implemented may affect the accuracy of pH data.

4.4.2 Electrical conductivity (EC)

Electrical conductivity was measured electrometrically using a Crison microCM 2201 EC meter with conductivity electrode and temperature sensor for temperature correction. EC values were reported at an ambient temperature of 20.5 °C.

4.4.3 Alkalinity

The acid neutralising capacity of the water was measured by end-point titration to pH 4.5 (Standard Methods, 1995) using standard 0.01M HCl and a Radiometer TTT85 auto titrator. The procedure involved determining the volume of HCl required to titrate an accurate volume of each sample to the end point pH. The first set of alkalinity determinations were performed using 5 mL of sample. These were followed by a second set of titrations carried out on 4 mL of sample.

In order to prevent suspended solids or precipitates from coating the glass electrode, deionised water was used to clean the electrode thoroughly in between titrations.

4.4.4 Dissolved organic carbon (DOC)

The technique used to determine the dissolved organic carbon content of the pore waters is based on the persulfate-ultraviolet oxidation method described by Standard Methods (1995). Pore water samples were filtered through 0.45 μm filters prior to analysis to prevent suspended solids from reducing the intensity of the ultraviolet light reaching the sample matrix.

The organic carbon was oxidised to carbon dioxide by persulfate in the presence of ultraviolet light. The CO_2 produced was passed through a semi-permeable membrane into a lightly buffered carbonate/bicarbonate mixture containing phenolphthalein solution. The intensity of the coloured solution was measured in a colorimeter in a flow cell. Potassium hydrogen phthalate standards of known organic carbon content were used to calibrate the concentrations of organic carbon in the interstitial water samples.

4.4.5 Nitrogen detected as ammonia

An automated colorimetric procedure was used to measure total ammonia-nitrogen (un-ionised NH_3-N plus ionised NH_4^+). Under the alkaline conditions (pH 8.0-11.5) ammonia reacted with hypochlorite to form monochloramine, which in the presence of excess hypochlorite and phenol, produced indophenol-blue. The reaction temperature was 65 °C.

The absorbance of indophenol-blue was measured at 630 nm. The precipitation of magnesium and calcium hydroxide was prevented by adding a complexing agent (trisodium citrate). Care was taken not to allow the pH to exceed pH 11, as this would have caused an erratic baseline. Maintaining the temperature at 65 °C prevents extra ammonia from being formed by the hydrolysis of nitrogen-containing compounds at higher temperatures. Details of the method are given in Grasshoff *et al.* (1983) and Kirkwood (1994).

4.4.6 Phosphorus detected as dissolved reactive phosphate

The concentration of dissolved reactive phosphate was determined on an automated system and is based on the colorimetric method described by Grasshof *et al.* (1983). Orthophosphate in the water samples was converted to phosphomolybdate by adding acidified ammonium molybdate. The reduction of phosphomolybdate by a combined potassium antimonyl tartrate and ascorbic acid reagent, produced an intense blue complex. Absorbance was measured at 880 nm.

A blank seawater sample was run to determine the influence of seawater on absorbance. This involved measuring the absorbance of the seawater sample without any reagents added to it. Care was taken not to use commercial detergent for washing glassware used in the phosphate determination, as detergents contain an excessive amount of phosphates (Grasshof *et al.*, 1983; Kirkwood, 1994).

4.4.7 Sulfate concentration

An automated procedure was used to determine sulfate. The sample was reacted with barium chloride in an acid medium to form barium sulfate. At low concentrations the sulfate precipitate exists as a colloidal suspension. The turbidity of the suspension is measured at 520 mμ. Silica over 400 ppm and colour in large amounts interfere (Technicon corporation, 1969). The automated procedure for the determination of sulfate is an adaptation of that described in Standard Methods (1965).

4.4.8 Chloride concentration

Chloride concentrations were determined using the automated ferricyanide method (Standard Methods, 1995). In the flow cell colorimeter, ferric nitrate solution was added to mercuric thiocyanate, producing mercuric chloride and a highly coloured ferric thiocyanate. The intensity of the latter product is proportional to the chloride concentration. The concentration range of 1 to 200 mg Cl^-/L can be extended by diluting the sample. There are no significant chemical interferences.

4.4.9 Major cations using FAAS

The total elemental concentrations of Na, Ca, Mg and K were determined by means of FAAS. All pore water samples were diluted with deionised water before being analysed on a Varian AA-1475 flame atomic absorption spectrophotometer.

4.4.10 Trace metals using FAAS

A liquid/liquid extraction technique was used to remove the interfering effects of the major seawater components, and to concentrate the dissolved trace metals in the sample. The metals were extracted from the water into chloroform using a mixed dithiocarbamate complexing agent (ammonium pyrrolidine dithiocarbamate and diethyl ammonium diethyl dithiocarbamate). The extracts were then evaporated at low heat and dissolved into nitric acid for analysis on a Varian AA-1475 flame atomic absorption spectrophotometer.

A combined stock standard solution containing the metals of interest, as well as reference seawater were analysed. The method was adapted from those used by Jones and Laslett (1994), and Magnusson and Westerlund (1981).

4.5 Results and discussion

The concentrations of the major components, pH values and EC values of the 13 pore water samples are presented in Table 4.1. Concentrations of nitrate and nitrite were not determined due to difficulties experienced with the column in the automated analyser. It is assumed, however, that since nitrate and nitrite are present early on in the diagenetic sequence for anoxic sediments, these forms of dissolved nitrogen would be present in low concentrations in most of the interstitial waters. The anion-cation charge balance of each water sample (Table 4.2) was calculated using the equation given by Murray and Wade (1996) as a measure of the quality of the analytical data. According to Murray and Wade (1996), anion-cation differences of about 2–5 % are considered acceptable for an anion range of 10–800 $mmol_c/L$. The anion-cation charge differences for the pore water samples range from 0.88 to 3.32 % and therefore the data can be considered to be of good quality.

Table 4.1 pH, EC and concentrations (mg/L) of major components in the pore waters of the Small Bay sediments.

Sample	pH	EC (mS/cm, 20.5 °C)	Salinity (‰)	Cl	Na	SO_4	Mg	Ca	K	Alkalinity (as HCO_3)	DOC	NH_3–N	PO_4–P
Typical seawater	[&]7.5–8.4		32–37	19387	11054	2780	1316	422	409	110	*0.3–2	[#]0.005–0.05	[#]0.001–0.10
PW1	7.9	53.8	40.06	22600	12000	2670	1070	604	542	570	24	59	0.23
PW2	7.9	52.0	40.39	22100	12200	3010	1130	708	542	698	22	26	18.0
PW3	7.7	49.6	37.06	20500	11300	2400	1040	552	480	783	37	50	12.0
PW4	7.8	52.0	39.29	22000	11800	3010	1080	604	506	290	<10	18	0.11
PW5	7.7	51.0	39.75	21400	12400	3520	1080	500	480	372	<10	26	0.02
PW6	8.2	50.3	39.18	22000	11800	2810	1080	552	480	457	16	38	0.23
PW7	7.9	51.0	39.47	22000	12200	2840	1080	450	490	410	10	29	0.02
PW8	7.7	54.0	43.29	23800	13000	3240	1190	656	646	757	40	82	9.00
PW9	7.9	50.1	39.01	21000	11700	3010	1100	604	646	948	85	99	17.0
PW11	7.7	46.6	35.77	19200	10800	2730	990	604	576	869	78	96	15.0
PW12	8.0	44.0	33.42	18300	10700	2340	975	430	440	230	<10	18	<0.01
PW13	7.8	47.5	36.39	20200	11200	2670	1020	450	455	394	11	41	0.02
PW14	8.5	45.1	34.76	19600	10700	2240	975	420	430	394	10	44	<0.01

Sources of typical seawater data: [&]Chester (1990); *Drever (1997); [#]Wheast (1969) and Millero (1996). Nitrogen concentrations are given in mg N/L, detected as NH_3 and NH_4^+; phosphorus concentrations are given in mg P/L, detected as PO_4^{3-}.

Table 4.2 Charge balance results for the pore water samples.

Sample	Sum of cations ($mmol_c/L$)	Sum of anions ($mmol_c/L$)	% difference
PW1	658	703	3.32
PW2	673	700	2.00
PW3	621	642	1.61
PW4	648	685	2.80
PW5	665	684	1.39
PW6	646	684	2.84
PW7	655	684	2.12
PW8	718	752	2.33
PW9	651	671	1.46
PW11	604	615	0.88
PW12	578	568	0.91
PW13	607	633	2.11
PW14	579	607	2.28

Charge balance equation used is according to Murray and Wade (1996): % difference = 100(Σcations-Σanions)/(Σcations+anions).

Throughout the discussion of the aqueous phase geochemistry, component concentrations in the pore waters are compared with those of typical seawater. Owing to the fact that coastal marine sediments are highly variable in composition, there is no data available pertaining to the composition of average nearshore interstitial waters. It is for this reason that average coastal seawater data has been used to highlight the existence of concentration gradients between the sediments and the overlying water. This data also serves to show similarities between typical seawater and the pore waters (in particular with respect to the major ion concentrations).

4.5.1 Salinity

The EC as well as summation of the major ions in a water sample represent estimations of salinity. The seven major ions (SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, Mg^{2+}, K^+ and HCO_3^-) were used in this calculation. The EC measurements range from 44 to 54 mS/cm with corresponding salinity values of between 33.42 and 43.29 ‰. All of the pore water samples have salinity values greater than that of average seawater

(~35 ‰), except PW12 and PW14, which have salinities of 33.42 and 34.76 ‰, respectively. Knesl (1996) and Lanz (1997) also found that sediment pore water salinities exceeded those of overlying bulk water in Barbers Pan (alkaline lake) and de Hoop Vlei (saline coastal lake) respectively.

Salinity in surface seawater ranges from about 32 to approximately 37 ‰ (Millero, 1996) and the major ions that contribute to salinity are usually conservative, meaning that their concentration ratios remain constant and their total concentrations can only be changed by physical processes. The high salinities of some of the pore water samples serve as an immediate indication that the concentrations of some of the major ions greatly exceed those of surface seawater.

Variations in salinity values between the samples may be related to the extent to which the respective sediments have undergone vertical mixing due to currents or bioturbation, as these physical processes can effectively dilute the interstitial waters (Libes, 1992).

4.5.2 pH

The pH data in Table 4.1 apply to pore water samples which had not yet been passed through a 0.45 m filter. All the samples are alkaline and they range from pH 7.7 to pH 8.5 (average pH is 7.9). This range is similar to the pH range of open-ocean seawater reported by Chester (1990) (~7.5 to ~8.4). The carbonate equilibria are responsible for stabilising the pH of seawater at approximately 8. Deviations can occur, however, which are the result of kinetic factors that inhibit the attainment of equilibrium (Libes, 1992). It is likely that the *in situ* pH values of the pore waters are slightly lower than those reported, due to the fairly high organic matter content of the sediments. The decomposition of organic matter produces CO_2, which is rapidly hydrolysed to form carbonic acid, bicarbonate and carbonate via the reactions (Libes, 1992),

$$CO_{2\,(aq)} + H_2O_{\,(l)} \leftrightarrow H_2CO_{3\,(aq)}$$

$$H_2CO_{3\,(aq)} \leftrightarrow H^+_{\,(aq)} + HCO_3^-{}_{(aq)}$$

$$HCO_3^-{}_{(aq)} \leftrightarrow H^+{}_{(aq)} + CO_3^{2-}{}_{(aq)}$$

Since H^+ is also produced, the generation of CO_2 can acidify the pore water. pH values as low as 6.8 have been measured in organic-rich sediments (pers. com., P. Monteiro). This process of acidification typically occurs in stagnant waters that contain large quantities of organic matter (which might include some estuaries and upwelling systems), where decomposition can produce acid faster than moving water can resupply carbonate buffers (Chester, 1990). The pH of the euphotic zone in a seawater body increases during the day and decreases at night. This can be explained by the net uptake of CO_2 that occurs during the day due to photosynthetically active organisms, and the net release of CO_2 at night due to dark respiration (Libes, 1992).

It is suggested that carbon dioxide may have escaped from the pore water samples during the squeezing process. This would account for the measured pH values being somewhat similar to the pH of typical seawater. Ideally, *in situ* pH measurements should be taken immediately after sediment collection to obtain more accurate results. The accuracy of the pH data may also be affected by the fact that buffer solutions were not matched to the ionic strength of the samples (as recommended by IUPAC). For the purpose of this discussion, however, it will be assumed that the available pH data are not grossly inaccurate.

4.5.3 Alkalinity

Alkalinity concentrations vary greatly between the pore water samples: concentrations of HCO_3^- range from 230 (PW12) to 948 mg/L (PW9). All the pore water samples contain significantly more bicarbonate than typical seawater (110 mg/L) does. The average HCO_3^- concentration is *ca.* 400 % higher than that of average seawater.

DOC is very strongly correlated with alkalinity in the pore waters at the 99 % confidence level (Spearman's R = 0.97; n=13). If the high alkalinities of the pore waters were attributed exclusively to extensive dissolution of $CaCO_3$, caused by high partial pressures of CO_2 produced by decomposing organic material, a correlation of

similar strength would be expected between DOC and dissolved Ca. In fact, a much poorer correlation exists between dissolved Ca and DOC (Spearman's R = 0.60; $p<0.05$; n=13). This suggests that the buffering system of the interstitial waters in Small Bay is not driven by calcium carbonate alone. The conjugate bases of weak acids may also contribute to the buffering ability of pore waters (Libes, 1992). Examples of such buffering reactions include:

$$H^+ + B(OH)_4^- \leftrightarrow B(OH)_3 + H_2O$$

$$H^+ + HPO_4^{2-} \leftrightarrow H_2PO_4^-$$

$$H^+ + H_3SiO_4^- \leftrightarrow H_4SiO_4$$

$$H^+ + NH_3 \leftrightarrow NH_4^+$$

Other reactions adding to the acid neutralising capacity of the pore waters could involve organic bases, and in anoxic waters, S^{2-} and HS^-.

4.5.4 Major ion chemistry

Molar concentrations of the major ions in the pore water samples, expressed as percentages, are presented in a bar chart in Figure 4.2. Proportions of the major ions do not vary considerably between samples. The dominant anion in each sample is chloride and the dominant cation is sodium. It is important to note that precipitates were observed in the pore water samples when removed from the refrigerator, prior to their being re-filtered for analysis. This indicates that some of the major ion concentrations measured in the samples may be slightly lower than the true interstitial water concentrations. It also highlights the fact that changes in temperature (as well as pH) greatly affect the precipitation and dissolution of mineral phases. The assumption is made, however, that the effects of these processes on the relative concentrations of the pore water components are fairly negligible.

Chloride concentrations range from 18300 to 23800 mg/L, with a mean concentration of 21131 mg/L. This value is *ca.* 9 % higher than that of average seawater. Chloride in seawater is a conservative anion (Bearman, 1989a).

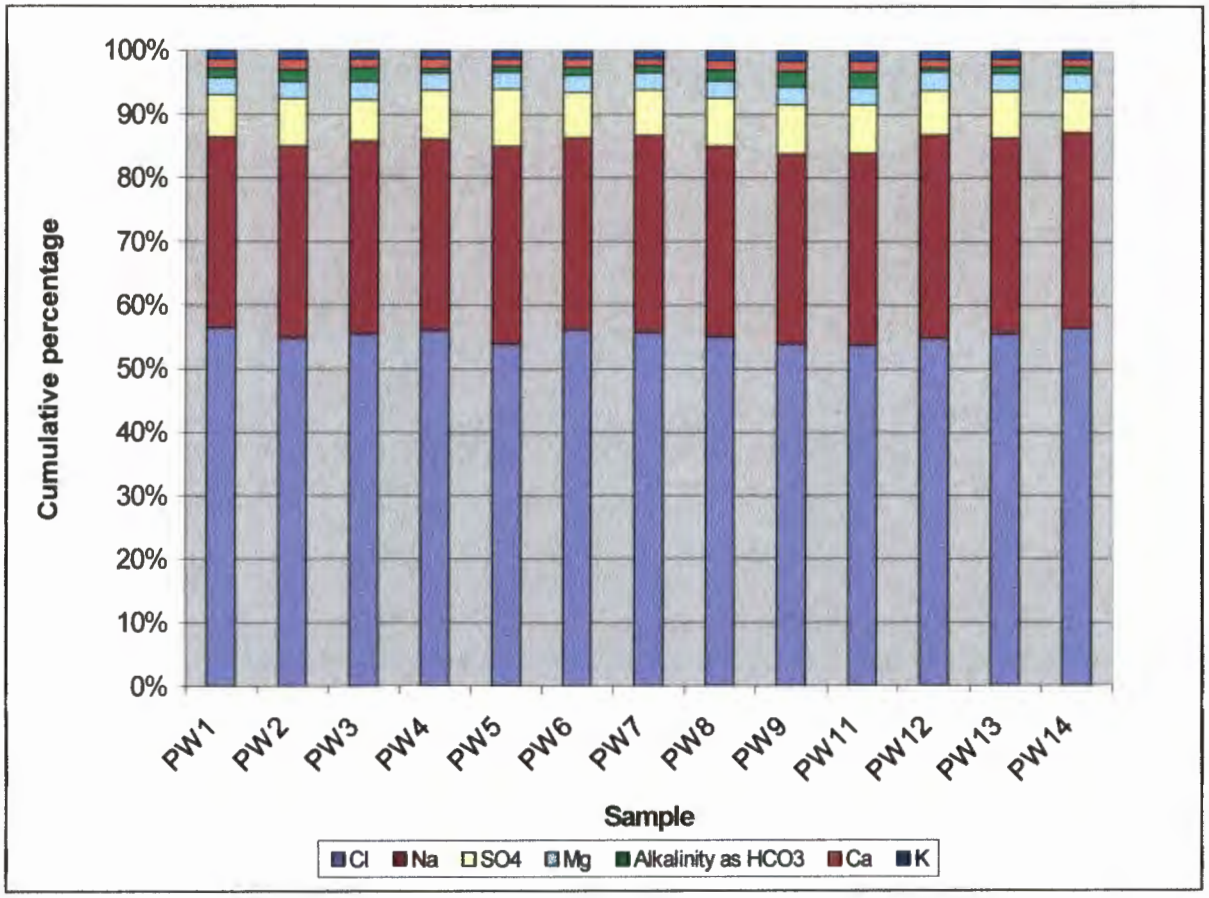


Figure 4.2 Molar concentrations of the major pore water ions expressed as percentages.

The dominant cation in the interstitial waters, sodium, ranges from 10700 to 13000 mg/L, and the average Na concentration of 11677 mg/L is *ca.* 6 % higher than that of typical seawater.

Sulfate concentrations range from 2240 to 3520 mg/L, with an average concentration of 2807 mg/L. This is *ca.* 1 % higher than that of typical seawater. Generally, sediment pore waters are found to contain less sulfate than normal seawater due to the production of H_2S by bacteria (Millero, 1996). Pore water samples containing more than 3000 mg SO_4^{2-}/L include PW5, PW8, PW2, PW4 and PW9. The relatively high sulfate level in PW5 is unexpected, as it was squeezed from a dark green/black muddy sediment which possesses one of the highest AVS concentrations (Table 3.2). It is suggested that much of the sulfide content of PW5 may have been oxidised to sulfate during the squeezing process. This would result in higher sulfate concentrations in the collected water.

Luther (1995) suggests that pore waters should be collected from Reeburgh squeezers in syringes to prevent the oxidation of reduced components. This would also prevent the outgassing of H_2S and other gases.

Magnesium concentrations range from 975 to 1190 mg/L. The average Mg concentration (1062 mg/L) is *ca.* 19 % less than that of typical seawater. Lower levels of Mg may be due to it being taken up by various clay minerals (such as chlorite) or by the Mg reacting with $CaCO_3$ to form dolomite. Magnesium is typically conservative in seawater Chester, (1990).

The average concentration of calcium in the interstitial waters (549 mg/L) is *ca.* 30 % greater than that of typical seawater. Dissolved Ca in the samples ranges from 420-708 mg/L. High Ca concentrations are likely to be the consequence of $CaCO_3$ dissolution caused by the oxidation of plant and other organic material, which produces CO_2. The solubility of carbonates in the pore water solution is dependent on the partial pressure of CO_2 (Drever, 1997) since dissolution is facilitated by the formation of bicarbonate:

$$CaCO_3(s) + H_2O(aq) + CO_2(g) \leftrightarrow Ca^{2+}(aq) + 2HCO_3^-(aq)$$

Pore water sample PW9 contains relatively high concentrations of Ca^{2+} and Mg^{2+} and the sediment core (C9) contained many large sand prawns. It is suggested that the high biological activity in this area can create a high partial pressure of CO_2, causing carbonates such as $CaCO_3$ and $MgCO_3$ to dissolve, and ultimately resulting in high aqueous concentrations of Ca^{2+} and Mg^{2+}.

The range of potassium concentrations in the interstitial water samples is 430-646 mg/L and the average level is 516 mg/L, which is *ca.* 26 % higher than K levels in typical seawater. Clay minerals, notably illite, could be responsible for the higher K content, by exchanging K^+ ions for other cations found in seawater, such as Na^+.

Table 4.3 contains ionic ratios calculated for the sediment interstitial waters. The sample ratios of Cl^-/Na^+ are very similar to that of typical seawater. Some of the

ratios are consistently higher or lower than the seawater value: the ratios of Na^+/K^- and Na^+/Ca^{2+} are lower than seawater for all samples, whereas Na^+/Mg^{2+}, K^+/Mg^{2+} and Ca^{2+}/Mg^{2+} are higher than typical seawater.

Table 4.3 Ionic ratios in the pore water samples.

Sample	Cl^-/Na^+	Na^+/K^+	Na^+/Mg^{2+}	Na^+/Ca^{2+}	K^+/Mg^{2+}	K^+/Ca^{2+}	Ca^{2+}/Mg^{2+}
Typical seawater	1.79	27.03	8.40	26.17	0.31	0.97	0.32
PW1	1.88	22.14	11.21	19.87	0.51	0.90	0.56
PW2	1.81	22.51	10.80	17.23	0.48	0.77	0.63
PW3	1.81	23.54	10.87	20.47	0.46	0.87	0.53
PW4	1.86	23.32	10.93	19.54	0.47	0.84	0.56
PW5	1.73	25.83	11.48	24.80	0.44	0.96	0.46
PW6	1.86	24.58	10.93	21.38	0.44	0.87	0.51
PW7	1.80	24.90	11.30	27.11	0.45	1.09	0.42
PW8	1.83	20.12	10.92	19.82	0.54	0.98	0.55
PW9	1.79	18.11	10.64	19.37	0.59	1.07	0.55
PW11	1.78	18.75	10.91	17.88	0.58	0.95	0.61
PW12	1.71	24.32	10.97	24.88	0.45	1.02	0.44
PW13	1.80	24.62	10.98	24.89	0.45	1.01	0.44
PW14	1.83	24.88	10.97	25.48	0.44	1.02	0.43

Ionic ratios for samples and typical seawater calculated using data presented in Table 4.1.

4.5.5 Dissolved organic carbon (DOC)

Dissolved organic carbon (DOC) constitutes approximately 50 % of the total dissolved organic matter (DOM). Other components of DOM include dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP). DOM is extremely complex and is present as a dilute mixture of compounds in seawater (Millero, 1996). Most DOM is produced *in situ* as a result of excretions and exudations from marine animals, microorganisms and plants (Libes, 1992). DOM has been well characterised with regard to CHN, total acidity, functional group analyses and molecular weight.

Levels of DOC range from <10 to 85 mg/L in the pore waters. In order to calculate the average DOC concentration in the samples, the DOC concentrations of PW4, PW5

and PW11 (all <10 mg/L) were taken as 5 mg/L for convenience. The mean concentration is 27 mg/L. The DOC content of the pore waters is significantly higher than that of typical seawater (0.3-2.0 mg/L), due to the sediments acting as a sink for organic matter. This is in accordance with the estimation that DOC in sediments is approximately ten times higher than in the overlying water (Buffle, 1988). Sample PW9 has the highest DOC and alkalinity concentrations (also high levels of K, N and P).

DOC in seawater is mainly related to primary productivity and concentrations are prone to seasonal fluctuations (Millero, 1996). Due to the bulk of organic material in the Small Bay sediments coming from the fish factories and the mussel beds in the area, fluctuations in pore water DOC levels are likely to depend mostly on the productivity of these operations.

4.5.6 Nutrients

Dissolved nitrogen and phosphorus occur in seawater as a result of the decomposition of organic matter. Since the sediments of Small Bay are generally in an anoxic state, most of the N and P in the pore waters can probably be attributed to the metabolism of organic material by anaerobic microorganisms. The denitrification and sulfate reduction reactions are (Libes, 1992):

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 84.8\ HNO_3 \rightarrow 106\ CO_2 + 148.8\ H_2O + 42.2\ N_2 + 16\ NH_3 + H_3PO_4$$

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 53\ SO_4^{2-} \rightarrow 106\ CO_2 + 106\ H_2O + 16\ NH_3 + 53\ S^{2-} + H_3PO_4$$

4.5.6.1 Nitrogen

Nitrogen in the pore waters was determined as NH_3 and NH_4^+. Ammonia in aqueous solution can exist in two forms, depending on pH. The dissociation of NH_4^+ is:

$$NH_4^+{}_{(aq)} \leftrightarrow H^+{}_{(aq)} + NH_3{}_{(aq)} \qquad (pK = 9.5 \text{ at } 25\ ^\circ C \text{ in seawater})$$

At the pH of seawater (approximately 8.2), 95 % of the total ammonia is present as NH_4^+ and 5 % as NH_3 (Millero, 1996). Ammonium and nitrates are produced during the oxic mineralisation of organic matter (Libes, 1992).

Concentrations of NH_3–N in the sediment pore waters range from 18 to 99 mg/L and the average concentration is 48 mg/L. All of the NH_3–N concentrations greatly exceed the range of NH_3–N levels in typical seawater. Such high concentrations suggest that the pore waters are anoxic.

The sediments also contain more organic material than typical seawater. Animals and microbes excrete low-molecular-weight compounds which tend to be rich in nitrogen (Libes, 1992). Such compounds include uric acid, urea, amino acids and nucleic acids. DOM is also released into seawater following the death of organisms and the microbial breakdown of faecal material. The sample with the highest NH_3–N concentration (PW9) was obtained from sediment containing many large sand prawns. Organic waste high in nitrogenous compounds may be responsible for the high dissolved N content. Variations in nitrogen concentrations among sediment samples containing large amounts of organic material may be partly attributed to the rate at which the dissolved matter is assimilated by organisms. Typically, these compounds have very high production rates but their concentrations in seawater are usually very low, due to rapid uptake by heterotrophic bacteria (Libes, 1992).

4.5.6.2 Phosphorus

Phosphorus (detected as phosphate) in the pore waters ranges from <0.01 to 18 mg/L. Concentrations reported as less than 0.01 mg/L (samples PW12 and PW14) were taken as 0.005 mg/L in calculating an average concentration (5.5 mg/L) for the 13 samples. This average concentration is higher than the upper value of the P range for typical seawater (Table 4.1) but only five out of the 13 samples (PW2, PW3, PW8, PW9 and PW11) are about two orders of magnitude greater than the upper limit of the range. Variation in the phosphorus concentrations is probably related to the differences in localised quantities of organic matter in the sediments. Sediments C2 and C3 contain fish debris from the fish factories and C8 and C9 probably contain

high proportions of organic waste coming from the mussel rafts. Elevated levels of P as well as N and DOC occur in PW11. Sediment sample C11 does not contain particularly high percentages of organic carbon or nitrogen (Figure 3.1). Hence, it is possible that significant quantities of organic matter are carried to this site by the clockwise current circulation in the Bay.

4.5.7 Trace metals

The concentrations of Fe, Mn, Cd, Cu, Pb and Zn in the sediment pore waters are presented in Table 4.4. Two sets of typical seawater concentrations are also given in Table 4.4. These data demonstrate the variation and difficulty involved in reporting average trace metal concentrations in seawater. Comparisons made in this section, between the sample concentrations and those of typical seawater, are referring to the higher of the two seawater values given in Table 4.4. Figure 4.3 contains a bar chart of the logged concentrations of Fe and Mn, and Figure 4.4 contains a bar chart in which the concentrations of Cd, Cu, Pb and Zn are displayed.

The concentrations of Fe in all the pore waters greatly exceed the Fe level in typical seawater. The sample concentrations range from 12 to 1242 μg/L , with a mean of 256 μg/L. Given that the pore waters are anoxic, most of the dissolved iron species are probably present as Fe(II) species. Since 0.45 μm filters were used to filter the pore water prior to metal analysis, it is likely that colloidal FeS accounts for a significant proportion of the Fe detected. It should also be noted that ferrihydrite ($FeOH_3$) exhibits very small particle sizes (1-10 nm) and is often colloidal in nature (Dzombak and Morel, 1990). Such material would also be able to pass through the 0.45 μm filters.

Manganese in the interstitial waters ranges from 1.64 to 8.24 μg/L and an average Mn concentration of 4.89 μg/L was calculated for the 13 samples. Manganese may be present in the form of colloidal MnS or as free Mn^{2+}. The minimum and maximum concentrations of Fe and Mn occur in the same samples: PW3 and PW8 respectively.

Table 4.4 Concentrations (μg/L) of trace metals in the pore water samples of Small Bay sediments.

Sample	Fe	Mn	Cd	Cu	Pb	Zn
Typical seawater	2 (0.055)	0.2 (0.1)	0.05 (0.1)	0.5 (0.1)	0.03 (0.002)	2 (0.5)
PW1	61	2.44	0.84	0.92	6.75	6.00
PW2	526	7.31	2.00	5.00	17.8	28.4
PW3	12	1.64	1.35	2.02	7.63	3.12
PW4	45	3.73	1.26	3.73	10.7	5.21
PW5	88	8.14	0.37	0.62	2.75	2.75
PW6	445	3.11	1.60	3.79	9.81	10.7
PW7	54	7.71	2.06	3.69	15.5	22.2
PW8	1242	8.24	2.64	65.9	15.5	15.0
PW9	393	4.26	0.68	44.3	4.02	10.9
PW11	399	3.17	0.95	37.4	6.55	130
PW12	16	3.75	0.07	0.39	2.16	10.1
PW13	30	2.46	0.18	0.46	1.00	1.91
PW14	14	7.61	0.13	41.8	2.23	47.9

Sources of typical seawater data are Drever (1997) and Bearman (1989b), the latter in parentheses.

Some of the Fe and Mn present in the sediment pore waters may be derived from the dissolution of Fe and Mn adsorption phases, mostly Fe and Mn sulfides. It is probable that a significant proportion of the Fe in solution can be attributed to the dissolution of particulate iron ore that has either been blown or spilled into the water in the vacinity of the ore jetty. Colloidal Fe derived from the ore may also be present. The concentration of Fe in all the pore water samples greatly exceeds that of Mn: dissolved Fe concentrations are on average approximately 50 times greater than dissolved Mn. Figure 4.3 provides a comparison of the logged concentrations of Fe and Mn in the interstitial water samples.

The processes that are responsible for Fe and Mn being in solution include those that control the dissolution and precipitation of Fe and Mn in marine sediments.

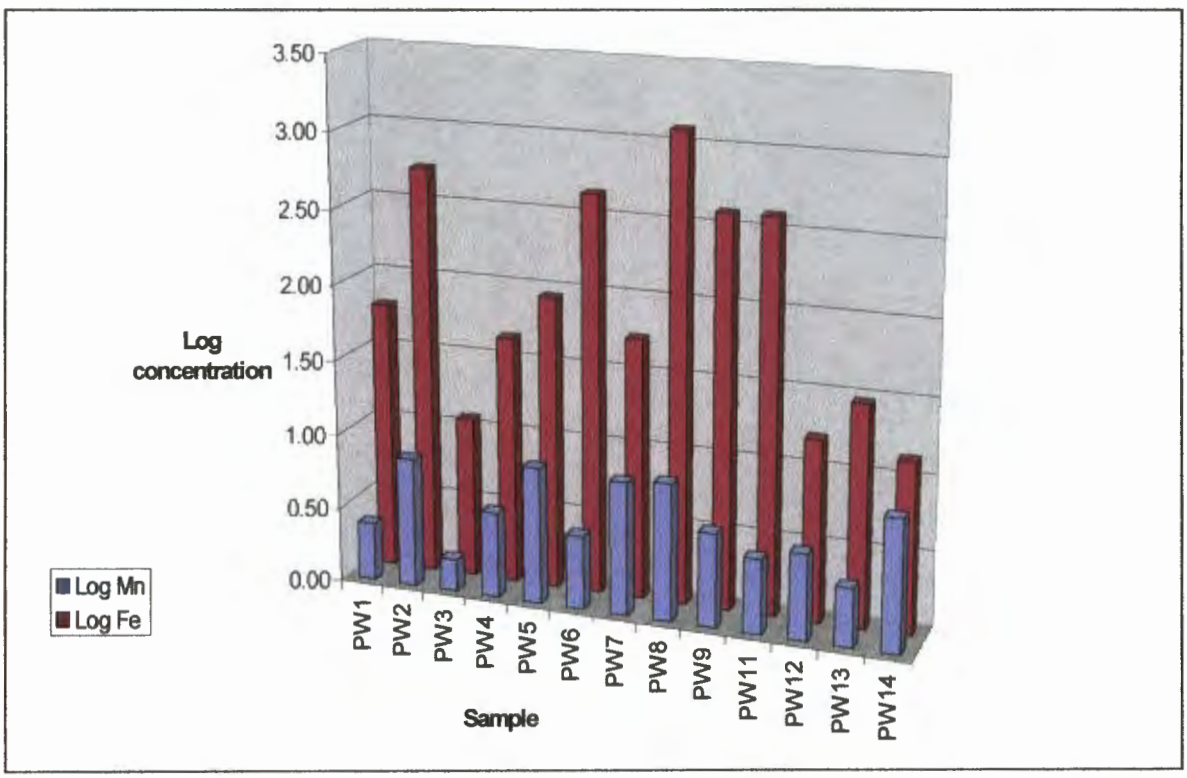


Figure 4.3 Concentrations of Fe and Mn in the pore waters.

It is generally accepted that only a small change in the solid phase due to mineral dissolution can have significant effects on the pore water concentrations of a metal (Luther, 1995). The dissolution of minerals in marine sediments can be caused by the bacterial decomposition of organic matter, by chemical reduction, chemical oxidation or by non-redox initiated dissolution (Luther, 1995).

Both Fe and Mn are reduced in sediments by the bacterial decomposition of organic matter. Reduction of these metals occurs readily, as oxygen and nitrate are not found in high concentrations, relative to the metal oxides (Luther, 1995). Reduction of Fe-oxide however, is less favourable than that of Mn and occurs later in the diagenetic sequence.

For the sulfides of iron, two processes are important in their dissolution. The first is the proton-mediated dissolution of FeS and the second is the oxidative dissolution of FeS_2. Pyrite does not dissolve significantly in acid because it is kinetically inert (Luther, 1995).

The concentrations of Cd, Cu, Pb and Zn in the sediment pore waters are shown graphically in Figure 4.4.

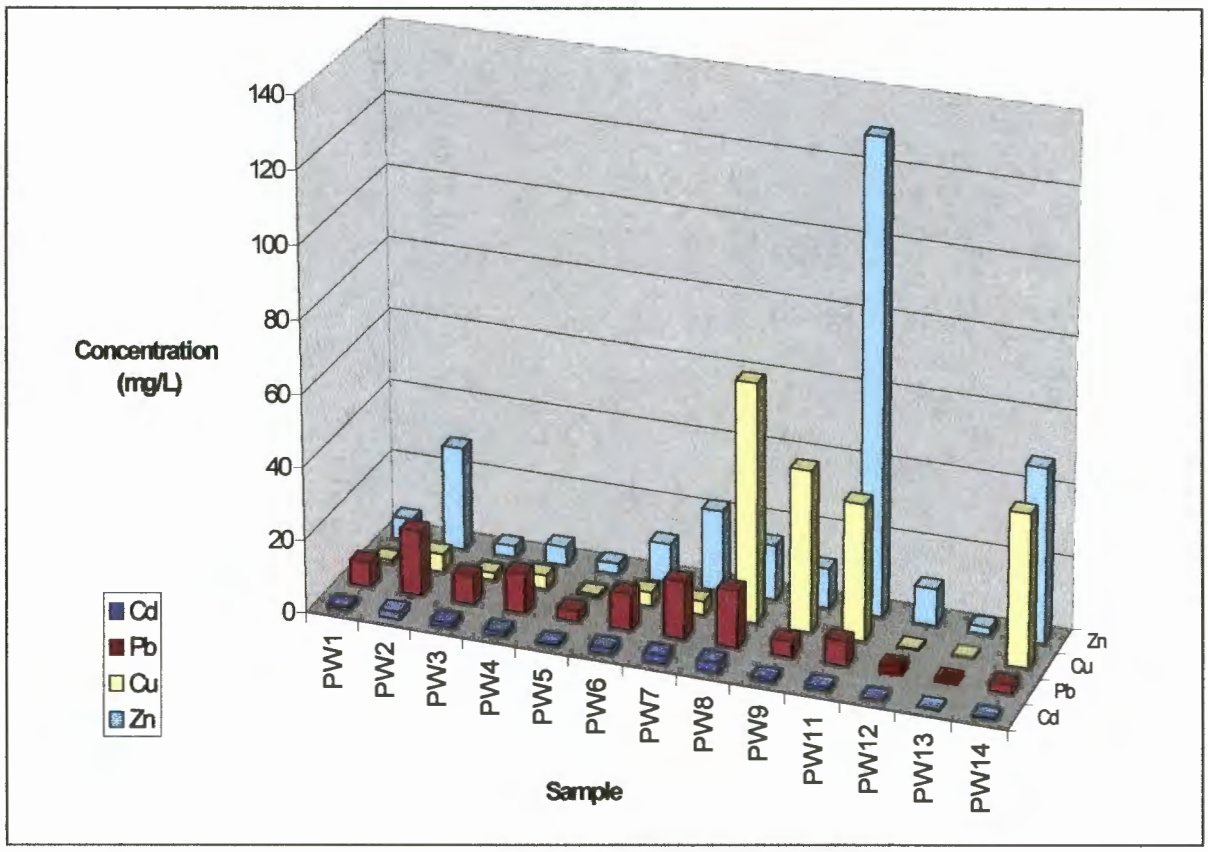


Figure 4.4 Concentrations of Cd, Cu, Pb and Zn in the sediment pore waters.

Cadmium concentrations range from 0.07 (PW12) to 2.64 μg/L (PW8). The average Cd level (1.1 μg/L) is approximately an order of magnitude greater than that of

typical seawater. The main Cd species likely to be present in the pore water is $CdCl_2$ but Cd may also be present as hydroxy species or as soluble $CdCO_3$. Anoxic samples may contain dissolved Cd-sulfide species. In ocean water, the distribution of Cd demonstrates a typical nutrient-type profile. There is depletion of the element in surface waters and a maximum near 1 km. This has been observed in the North Pacific and North Atlantic (Millero, 1996). Cadmium is removed from the surface waters by plankton or organic particulate matter and is regenerated in deeper waters when the particulate matter is oxidised by bacteria. This behaviour suggests that Cd can be associated with the soft parts of living and dead biological material (Millero, 1996). Given the high organic content of the Small Bay sediments and the fairly high pH of the samples, it is possible that a significant proportion of dissolved Cd in the interstitial waters is associated with soluble organic species.

Copper concentrations in the pore waters range from 0.39 (PW8) to 65.9 μg/L (PW12). The average Cu concentration for the samples (16.2 μg/L) is about 32 times greater than that of typical seawater. Most of the soluble Cu in the pore waters is likely to be present in the form of Cu-organic complexes with some as $CuCO_3$, $CuOH^+$ or as free Cu^{2+}. Colloidal copper sulfide species may also be present in the anoxic water samples. The adsorption of Cu^{2+} on living or dead bacteria is well known (Millero, 1996). Scavenging of Cu is likely to be the result of ionic interactions with surface –OH and –COOH groups on the organic matter (Millero, 1996).

It is important to note that sample PW8 contains the highest concentrations of dissolved Fe, Mn, Cd and Cu as well as one of the highest Pb concentrations. Sediment C8 was collected in the area of the mussel beds, near the entrance to Small Bay. It is possible that due to the clockwise circulation of surface water in Small Bay and the acceleration of this water in a south-westward direction along the iron-ore causeway (CSIR, 1995), dust from the metal concentrates and iron ore is being carried to the entrance of Small Bay and settling there. This would not explain, however, the significantly lower Fe concentrations in PW7 and PW9, which were obtained from sediments at neighbouring sites. Another possible source of

metals in PW8 may be the metal components of the mussel rafts, which corrode and accumulate in the sediments.

Concentrations of lead in the pore waters range from 1.00 (PW13) to 17.8 μg/L (PW2) and the average is 7.9 μg/L. All samples exceed the Pb concentration of typical seawater. Lead detected in the pore waters is probably in the form of $PbCO_3$, $Pb(CO_3)_2^{2-}$, $PbCl^+$ and Pb-organic species. Colloidal Pb-sulfides may be present in the anoxic interstitial waters.

The average Pb concentration in the pore waters is two orders of magnitude greater than that of typical seawater. A likely source of Pb in the Bay would be red PbO which is used in primer paints to prevent corrosion on boats. The highest pore water Pb concentration is found in PW2. Sediment C2 was collected from the fish factory area of Small Bay which is often very busy with fishing boats and other sea vessels. An additional source of contamination may be the exhausts of motor vehicles and ships. Lead is injected into the atmosphere in the form of an aerosol by the burning of leaded petrol. Particulate lead is washed out of the atmosphere and onto the sea surface by rain, where it can adsorb onto sinking particulate matter. Libes (1992) reports that since the use of leaded petrol in the United States has declined, surface water concentrations have decreased.

Zinc concentrations in the pore waters range from 1.91 (PW13) to 130 μg/L (PW11). The average Zn concentration is 22.6 μg/L. When the concentration of PW11 is excluded, the average concentration is calculated as 13.7 μg/L. The latter concentration is approximately seven times greater than that of typical seawater. Sample PW11 was obtained from the northern-most corner of Small Bay. Zinc is likely to be present as Zn^{2+}, $ZnOH^+$, $ZnCO_3$ and $ZnCl^+$ in the interstitial waters. Some colloidal Zn-sulfide species may also exist in the anoxic water samples.

The pore water parameters which have the most influence on the mobility of Cd, Cu, Pb and Zn in the sediments will be discussed in more detail in Chapter 5.

4.6 Conclusions

All the pore water samples are more saline than typical seawater. Electrical conductivities range from 44 to 54 mS/cm, with a corresponding salinity range of 33.4 to 43.3 ‰. This is an immediate indication that the concentrations of the major ions in the pore waters are generally higher than those of typical seawater.

The pH of the interstitial waters is alkaline and ranges from 7.7 to 8.5. This range is similar to that for open-ocean water but is atypical of organic-rich sediments, since the mineralisation of organic material has an acidifying effect.

Alkalinity, as bicarbonate, demonstrates considerable spatial variation. Concentrations of HCO_3^- range from 230 to 948 mg/L and all samples have higher alkalinity than typical seawater (110 mg/L). A very strong correlation exists between DOC and alkalinity but the correlation between DOC and dissolved calcium is considerably poorer. This indicates that the buffering system of the sediments is not controlled by $CaCO_3$ alone. Other proton-accepting species must be contributing to the high alkalinities of the pore waters. Such species could include the conjugate bases of weak acids, organic bases, and in anoxic waters, HS^- or S^{2-}.

The proportions of the major ions do not vary considerably between samples. The dominant cation and anion are obviously Na^+ and Cl^- respectively. The ratios of Cl^- to Na^+ are very similar to that of average seawater. The following major ions are present in the pore waters at higher concentrations than those of typical seawater: Cl^-, Na^+, SO_4^{2-}, Ca^{2+} and K^+. The average Mg^{2+} pore water concentration is 19 % less than that of normal seawater. This may be due to the uptake of magnesium by clay minerals or by $CaCO_3$ to form dolomite. Chloride, sodium and sulfate are only slightly more concentrated in the interstitial waters. Calcium pore water concentrations are significantly higher than that of typical seawater (the average Ca concentration of 549 mg/L is higher by 30 %). This has been attributed to the oxidation of organic material in the sediments, which produces CO_2 and causes the dissolution of $CaCO_3$. The average potassium concentration in the interstitial waters is about 26 % higher than the level of K found in normal seawater.

The sediments of Small Bay are effectively acting as a sink for organic material, and this is reflected clearly by the nutrient concentrations of the pore waters. DOC concentrations range from less than 10 to 85 mg/L, with an average concentration of 27 mg/L, which is roughly 14 times greater than the amount of DOC in typical seawater.

The average NH_3–N concentration is approximately 960 times higher than normal seawater. NH_3–N concentrations range from 18 to 99 mg/L. These high concentrations reflect the anoxic condition of the interstitial waters.

Phosphorus concentrations vary widely in the pore waters but they are generally highest in the samples from the fish factory zone and the mussel bed area.

Sample PW9 contains the highest levels of DOC, N and one of the highest P concentrations. These may be related to the close proximity of the mussel beds.

The dissolved organic carbon and phosphate in the sediment pore waters represent a significant supply of organic ligands available for complexing trace metals and increasing their solubility in the sediment environment.

Of the trace metals in the pore waters, Fe, Cd, Cu and Zn show tremendous ranges in concentration. Iron concentrations range from 12 (PW3) to 1242 μg/L (PW8). Excluding the maximum concentration of 1242 μg/L, the average Fe level is 174 μg/L, which is still considerably higher than the concentration of typical seawater.

Manganese concentrations range from 1.64 to 8.24 μg/L. The highest Mn and Fe levels are found in PW8 and the lowest Mn and Fe concentrations occur in PW3.

Concentrations of cadmium (0.07-2.64 μg/L), copper (0.39-65.9 μg/L) and zinc (1.91-130 μg/L) span a two-order of magnitude range. The average concentrations of Cu, Pb and Zn are considerably higher than the respective typical seawater concentrations.

Sample PW8 contains the highest concentrations of Fe, Mn, Cd and Cu, as well as one of the highest Pb concentrations. The clockwise-moving surface currents in Small Bay may be responsible for carrying metal concentrate dust from the jetty area to the mussel bed zone. Another possible source is the metal mussel rafts. It is likely that additional sources of lead, such as the burning of leaded petrol in fishing boats and other vessels, may contribute to the lead content of the sediments.

CHAPTER 5

Metal partitioning

5.1 Introduction

The distribution or mobility of trace metals in sediments can be investigated by applying the equilibrium partitioning concept, which has been reviewed in section 2.7. This approach assumes that trace metals are in equilibrium with respect to the solid and solution phases of the sediment and the partitioning of trace metals between these compartments can be predicted based on partition coefficients.

The aims of this chapter are to investigate the relationships between the calculated partition coefficients for Cd, Cu, Pb and Zn and characteristics of the sediment system, and to apply the empirical (statistical) approach (section 2.7.2) to predict partition coefficients for the Small Bay sediments. A further aim is to identify the distinguishing variables in the sediments (using Principal Component Analysis (PCA)), as these may aid in explaining the distribution of trace metals between the sediment compartments.

5.2 Partition coefficients

Field-based partition coefficients (K_p) were determined for Cd, Cu, Pb and Zn by calculating the ratio of the amount of the metal digested by nitric acid, perchloric acid and hydrogen peroxide (Table 3.7) to the concentration in the pore water (Table 4.4). The calculated partition coefficients are presented in Table 5.1 and they are displayed in bar charts in Figure 5.1. For a given metal, K_p varies significantly among samples but for a given sample, the variation among K_p values is considerably less.

Copper displays the largest range in calculated partition coefficients. Sample C8 shows the lowest K_p (Cd) as well as the lowest K_p (Cu). The highest Cu, Pb and Zn partition coefficients were found in sample C5.

Table 5.1 Calculated partition coefficients for Cd, Cu, Pb and Zn.

Sample	K_p **(Cd)** (L/kg)	K_p **(Cu)** (L/kg)	K_p **(Pb)** (L/kg)	K_p **(Zn)** (L/kg)
C1	2700	38800	14900	35200
C2	360	2000	900	730
C3	580	5500	2100	9100
C4	850	1700	3900	3200
C5	5200	221000	93100	98800
C6	980	2400	4100	3600
C7	1100	3200	2600	2600
C8	290	70	1900	450
C9	840	110	7500	400
C11	580	170	4400	40
C12	7800	23200	19800	1200
C13	4200	21600	42700	7200
C14	16600	700	19300	1400
Range	290-16600	70-221000	900-93100	40-98800
Mean	3237	24650	16708	12609
s.d.	4625	60212	25774	27542

Cadmium partition coefficients range from 290 (C8) to 16600 L/kg (C14); K_p (Cu) ranges from 70 (C8) to 221000 L/kg (C5); K_p (Pb) ranges from 900 (C2) to 93100 L/kg (C5) and K_p (Zn) ranges from 40 (C11) to 98800 L/kg (C5).

For each metal the standard deviation in K_p values greatly exceeds the mean. This is due to the presence of outliers in the K_p data and it reflects the extent to which the data

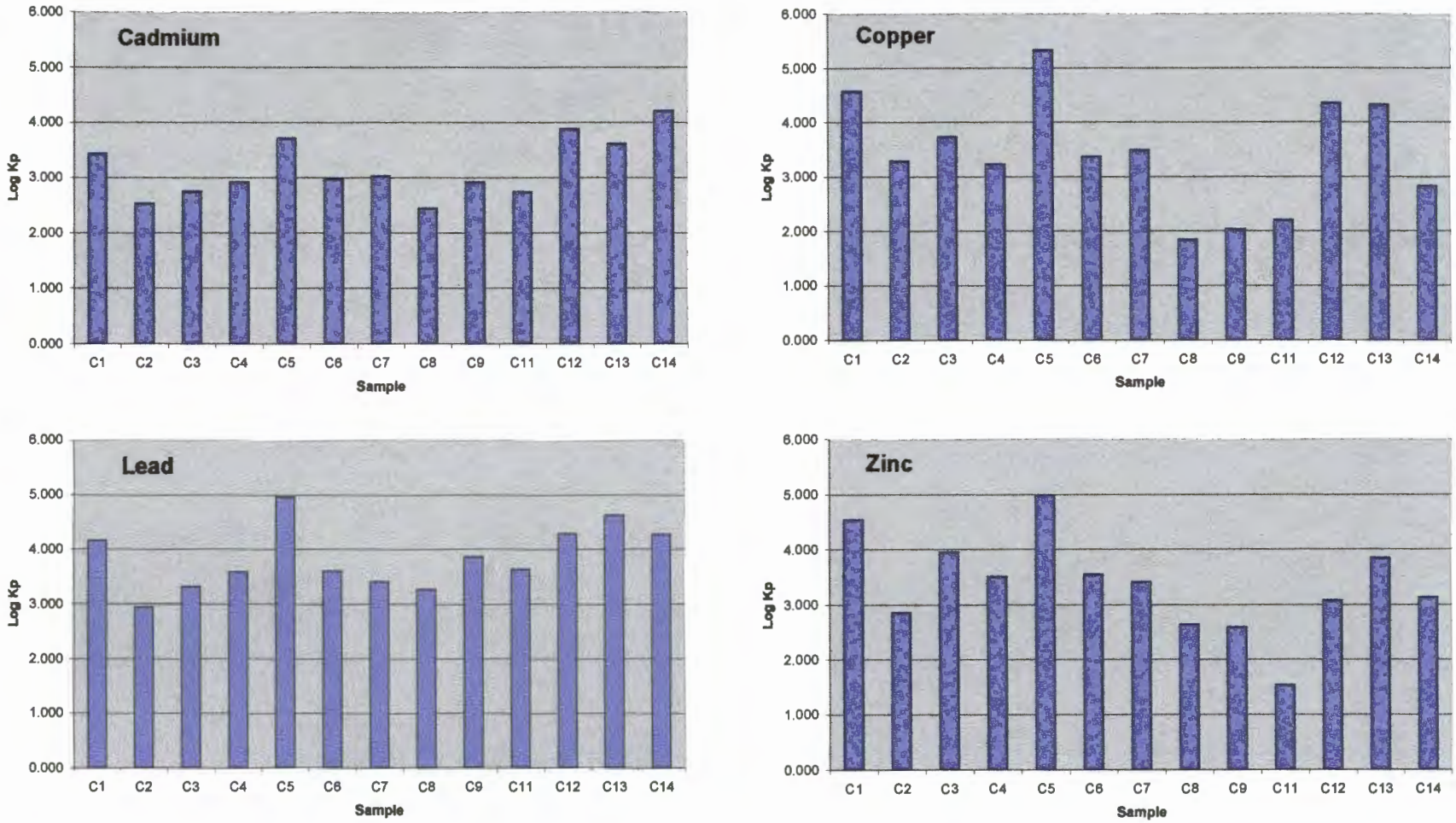


Figure 5.1 Log partition coefficients of cadmium, copper, lead and zinc for the sediments in Small Bay.

In order to investigate the relationships between the calculated partition coefficients and various sediment characteristics, a Pearson's product moment correlation analysis was performed on log-transformed data (except pH). Variables selected to represent the sediment solid phase were OC (organic carbon in the humic and fulvic acid fraction), AVS, and the oxyhydroxides of Al, Fe and Mn (abbreviated in this discussion to Al-oxy, Fe-oxy and Mn-oxy). The aqueous phase variables selected for the correlation analysis were phosphorus, alkalinity, DOC, pH, sulfate and chloride. The results of the analysis are presented in Table 5.2.

K_p (Cd) is positively correlated with AVS at the 95 % confidence level (a correlation was also found to exist between elemental S and Cd at the 99 % confidence level, Table 3.8). This is not surprising, since cadmium is a chalcophile element (McBride, 1994; Alloway, 1995a). The concentration of cadmium in the solid phase is therefore increased by the formation of Cd-sulfides. K_p (Cd) is also positively correlated with K_p (Cu) and K_p (Pb), the latter being a very strong association (r=0.85).

Negative correlations exist between K_p (Cd) and three of the aqueous phase components in Table 5.2 : phosphorus, alkalinity and DOC. Given that the alkalinity of the pore waters represents a range of dissolved species including phosphate, S^{2-}, HS^- and carbonate, it is suggested that the mobility of Cd in the sediments is increased by the formation of soluble phosphate, sulfide, carbonate and organic species. The negative relationship between K_p (Cd) and P is highly significant (Pearson's R=0.85).

K_p (Cu) is positively correlated with K_p (Cd), K_p (Pb) and K_p (Zn). The correlation between K_p (Cu) and AVS is almost significant at the 95 % confidence level (p=0.052). Like K_p (Cd), K_p (Cu) is significantly negatively correlated with P, alkalinity and DOC. The correlations between DOC and the partition coefficients of these two metals are of similar strength.

Table 5.2 Pearson's product moment correlation matrix for partition coefficients and selected variables of the sediment solid and aqueous phases (n=13). All data (except pH) are log-transformed.

	K_p (Cd)	K_p (Cu)	K_p (Pb)	K_p (Zn)	#OC	AVS	*Al-oxy	*Fe-oxy	*Mn-oxy	pH	SO_4	Cl	P	ΦAlk	DOC
K_p (Cd)	1.00														
K_p (Cu)	0.55	1.00													
K_p (Pb)	0.85	0.61	1.00												
K_p (Zn)	0.42	0.85	0.51	1.00											
#OC	-0.35	0.14	-0.22	0.43	1.00										
AVS	0.75	0.57	0.65	0.52	-0.03	1.00									
*Al-oxy	-0.48	-0.11	-0.41	0.05	0.12	-0.57	1.00								
*Fe-oxy	-0.30	0.31	-0.25	0.31	0.31	0.04	0.59	1.00							
*Mn-oxy	0.03	0.16	-0.12	0.27	0.05	0.10	0.68	0.77	1.00						
pH	0.54	-0.08	0.14	-0.04	-0.13	0.36	-0.26	-0.35	0.12	1.00					
SO_4	-0.46	-0.04	-0.07	0.12	0.40	-0.13	0.12	0.17	-0.20	-0.54	1.00				
Cl	-0.54	-0.12	-0.40	0.26	0.66	-0.15	0.23	0.16	-0.01	-0.24	0.66	1.00			
P	-0.85	-0.59	-0.67	-0.47	0.06	-0.86	0.68	0.25	0.08	-0.46	0.30	0.31	1.00		
ΦAlk	-0.67	-0.58	-0.50	-0.42	0.04	-0.63	0.57	0.21	0.12	-0.32	0.20	0.27	0.90	1.00	
DOC	-0.61	-0.66	-0.47	-0.55	-0.06	-0.68	0.41	-0.02	-0.09	-0.25	0.04	0.12	0.86	0.96	1.00

#OC is the organic carbon in the humic and fulvic acids (NaOH extraction); *The suffix "-oxy" denotes oxyhydroxides;ΦAlk denotes alkalinity;Shaded correlation coefficients are significant at the 95 % confidence level.

The mobility of Cu in the sediments of Small Bay is also likely, therefore, to be increased by the formation of soluble copper phosphate, carbonate and organic species.

K_p (Pb), however, shows a significant negative correlation only with phosphorus at the 95 % confidence level, but is positively correlated with AVS. This suggests that the formation of lead phosphate increases Pb mobility and sulfides play a significant role in reducing the mobility of lead in the sediments of Small Bay. K_p (Pb) is also significantly correlated with K_p (Cd) and K_p (Cu).

The negative correlation between K_p (Zn) and DOC is weaker than the relationships between DOC and the partition coefficients of Cd and Cu. A significant correlation exists between K_p (Zn) and K_p (Cu) at the 95 % confidence level.

None of the partition coefficients is significantly correlated with the oxyhydroxides (Al, Fe or Mn) at the 95 % confidence level. The same is true for OC, but the existence of negative relationships between DOC and K_p (Cd), K_p (Cu) and K_p (Zn), suggests that complexation by soluble organic species increases the concentrations of these metals in the sediment aqueous phase.

In Table 5.3 the ranges of the metal partition coefficients found in the Small Bay sediments are compared with those determined in other studies for marine surface waters. The ranges in K_p values are generally much greater in the Small Bay sediments than in the other systems. Although salinity varies significantly in estuarine environments, it is probable that both the solid and aqueous phases of the Small Bay sediments are more variable in composition than those of the surface seawaters .

The lower limits of the K_p ranges in the present study are consistently lower than those of the other investigations referred to in Table 5.3. The occurrence of lower metal concentrations in the solid phase of the Small Bay sediments may be a consequence of the oxidation of reduced metal sulfides during the sediment squeezing process. It

may also be attributed to the particularly high concentrations of dissolved organic species and phosphate in some of the pore waters, as these ligands can effectively scavenge trace metals (Buffle, 1988; Chester, 1990).

General trends observed in the other three studies are that lead has the greatest affinity for the particulate phase and cadmium the greatest affinity for the dissolved phase. These trends are also observed in the sediment system of Small Bay, as indicated by the upper and lower limits of the K_p (Cd) and K_p (Pb) ranges, respectively.

Table 5.3 Comparison of log K_p values from Small Bay sediments with K_p values of surface waters from other studies (units of raw data are L/kg).

	Small Bay Sediments	Seine estuary [a]	British coast [b]	Scheldt estuary [c]
Cd	2.5 – 4.2	3.9 – 4.0	3.5 – 5.0	4.5 – 5.0
Cu	1.9 – 5.3	4.5 – 4.7	4.0 – 5.0	4.8 – 5.0
Pb	3.0 – 5.0	6.1 – 6.3	5.0 – 7.0	6.2 – 6.5
Zn	1.5 – 5.0	4.4 – 4.7	4.0 – 5.0	Na

[a] From Chiffoleau et al. (1994);

[b] From Balls (1989);

[c] From Valenta et al. (1986);

na : data not available.

5.2.1 Predicting partition coefficients

In following the empirical approach to predicting partition coefficients, multiple linear regression can be used to express the calculated partition coefficients in terms of regression equations, incorporating sediment variables and corresponding weighting factors.

The use of multivariate regression requires that, in addition to the data showing normal distribution, the independent variables must be uncorrelated with one another. If they

are not, collinearity is said to exist (Johnston, 1991). The assumption of normality could be met by using log-transformed data (except pH). Relationships between the selected sediment variables were investigated by performing a correlation analysis (Table 5.2). Collinearity is indicated by the numerous correlations between the variables. A discussion of some of these correlations follows.

At the 95 % confidence level, AVS is negatively correlated with P, DOC, alkalinity and Al-oxy. Co-variance may be involved in some of these apparent relationships.

The positive correlations between P, alkalinity and DOC are highly significant at the 95 % confidence level. The strongest correlation among these three variables is that between alkalinity and DOC (Pearson's R = 0.96). This may be partially due to the facilitation of $CaCO_3$ dissolution by increased CO_2 partial pressure, caused by the decomposition of organic matter. It may also be attributed to the acid neutralising capacity of organic bases in seawater. Phosphate is a product of the decomposition of organic material.

The hydrous oxides of Al, Fe and Mn are all positively correlated with one another at the 95 % confidence level. The strongest relationship among these variables is that between Fe-oxy and Mn-oxy (Pearson's R = 0.77). Iron and Mn oxyhydroxides are ubiquitous in sediments which are not strongly reducing (Hall *et al.*, 1996; Drever, 1997). Hence, due to the highly anoxic nature of the sediments in Small Bay, it is very unlikely that Fe and Mn will exist as hydrous oxides, but rather in the form of Fe and Mn sulfides. As has been discussed previously, the hydroxylamine hydrochloride/HCl extractions are insufficiently selective to only digest metals which are in the form of amorphous hydrous oxides. Nevertheless, the log concentrations of Al, Fe and Mn in the hydroxylamine hydrochloride/HCl extractions are strongly correlated and thus, these variables are collinear.

The fairly strong correlation between sulfate and chloride can be explained by the fact that both of these components are major constituents of seawater. A very strong

correlation is not expected, however, since chloride is considerably more conservative in sediments than sulfate (due to the formation of sulfides).

5.3 Principal component analysis (PCA)

Principal component analysis was performed on log-transformed data (OC; AVS; Al-oxy; Fe-oxy; Mn-oxy; pH; sulfate; chloride; phosphorus; alkalinity and DOC) using STATISTICA software. The PCA results are presented in Table 5.4.

Table 5.4 Results of the Principal Component Analysis: factor loadings (unrotated) and eigenvalues.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
OC	0.242	0.633	-0.399	-0.418	-0.102
AVS	-0.768	0.402	0.052	0.030	0.480
Al-oxy	0.766	0.224	0.479	-0.038	-0.261
Fe-oxy	0.410	0.690	0.462	0.230	0.152
Mn-oxy	0.215	0.529	0.797	-0.083	0.030
pH	-0.546	-0.146	0.308	-0.708	0.022
SO_4	0.411	0.410	-0.652	0.235	0.081
Cl	0.452	0.497	-0.544	-0.355	0.031
P	0.961	-0.239	0.016	0.002	-0.026
Alkalinity	0.885	-0.281	0.071	-0.139	0.333
DOC	0.778	-0.524	0.017	-0.160	0.283
Eigenvalue	4.431	2.216	2.061	0.963	0.532

The PCA of the data shows that 93 % of the total variance is explained by the first 5 multi-variate factors, with 40 % explained by the first factor and 60 % by the first two factors. The variable loadings on the factors indicate that the first factor reflects two components in the solid phase, AVS and Al-oxy, and three components of the aqueous phase, P, alkalinity and DOC. A high negative loading occurs for AVS and a high positive loading for Al-oxy. The high loadings for phosphorus, alkalinity and DOC

are all positive. Phosphorus and alkalinity are related to the decomposition of sediment organic matter. DOC represents dissolved organic species in the pore water.

The second factor shows two fairly high positive loadings: these are for Fe-oxy and OC.

Factor 3 reflects one component of the solid phase and one of the aqueous phase. A high positive loading is shown for Mn-oxy and a fairly high negative factor is shown for sulfate.

Factor 4 reveals a high negative loading for the pH of the aqueous phase.

The PCA, therefore, shows that the most distinguishing variables in the sediments are AVS, Al-oxy, Fe-oxy, Mn-oxy, dissolved products of organic matter decomposition (P and alkalinity) and particulate as well as dissolved organic matter (OC and DOC).

5.4 Conclusions

For each metal, the calculated K_p values vary significantly among the samples but for a given sample, the variation between the partition coefficients is considerably less.

K_p (Cd) correlates well with sulfide content and it is suggested that the Cd partition coefficients are increased by the formation of insoluble sulfides and are lowered by the formation of soluble Cd-phosphate, Cd-sulfide, Cd-carbonate and organo-cadmium species.

K_p (Cu) is also decreased by the formation of dissolved phosphate, carbonate, sulfide and organic species.

K_p (Pb) correlates well with AVS and the mobility of Pb appears to be increased by the formation of soluble Pb-phosphate species.

CHAPTER 6

Conclusions

The objectives of this study were outlined in a number of key questions posed in the Introduction. Answers to these questions, based on the findings of this study, are presented in this chapter.

♦ **What are the concentrations of Cd, Cu, Pb and Zn in the sediments and how are these metals distributed?**

Cadmium concentrations in the sediment solid phase range from 0.55 (C11 and C12) to 2.31 mg/kg (C1) and the average Cd level is 1.23 mg/kg.

The highest concentrations of solid phase copper, lead and zinc were all detected in sample C5 and the lowest in either C8 or C9. Copper concentrations range from about 5 (C9) to 143 mg/kg (C5). Excluding the outliers C1, C5 and C14, the average Cu concentration is 9.3 mg/kg.

Solid phase lead concentrations range from less than 4.6 (C8) to 287 mg/kg (C5). The average lead concentration is about 20 mg/kg when the outlier C5 is excluded.

Levels of zinc in the solid phase range from 10 (C9 and C11) to 279 mg/kg (C5). An average concentration of approximately 36 mg/kg is calculated for the sediments when the outliers C1 and C5 are excluded.

Sample C5 (which contains enormously high concentrations of solid phase Cu, Pb and Zn) was collected near the fish factories, in a relatively sheltered area of Small Bay.

Pore water concentrations of cadmium (0.07-2.64 μg/L), copper (0.39-65.9 μg/L) and zinc (1.91-130 μg/L) span a two-order of magnitude range. The average concentrations of Cu, Pb and Zn are considerably higher than the respective typical

seawater concentrations. Levels of lead in the pore waters range from 1.00 to 17.8 μg/L.

Sample PW8 contains the highest concentrations of Cd, Cu as well as one of the highest Pb concentrations. This pore water sample was obtained from the mussel raft area of Small Bay.

♦ **To what extent are the sediments being contaminated with these metals?**

Previous studies have highlighted the trace metal contamination of the Small Bay sediments. The data obtained in this study can be used to determine if the contamination is worsening.

Previous studies have only reported average trace metal concentrations for the sediments of Saldanha Bay. Since the number of sediment samples used in this study is relatively small, it is more appropriate to exclude obvious outlier concentrations when calculating average concentrations.

Concentrations of cadmium and lead in the sediments, prior to the development of the bay for iron ore and metal concentrate export, are not known. However, since 1977, levels of copper and zinc have increased ten-fold and five-fold, respectively.

Average concentrations of Cd, Cu, Pb and Zn have all increased slightly over the past 15 years. Since 1983, cadmium concentrations have increased about three-fold, copper levels nearly three-fold, lead almost four-fold and zinc approximately three-fold.

It can, therefore, be concluded that the metal contamination in Saldanha Bay has worsened slightly since the early eighties. Recent dredging near the ore and metal concentrate jetties may have improved the condition of the bay by removing substantial quantities of contaminated sediment. Due to the continuing industrial development in the area of Saldanha Bay, it is likely that the metal contamination of the sediments will become more severe.

♦ **What factors control the mobility of these metals in the sediments?**

Although it was not possible to derive expressions for describing the metal partition coefficients in terms of the sediment characteristics, correlation analyses allowed for the identification of significant relationships between the coefficients and certain variables.

Cadmium mobility appears to increase by the formation of soluble phosphate, carbonate and organic species. Mobility is reduced by the formation of insoluble Cd-sulfides.

Like cadmium, the mobility of copper is increased by the formation of carbonate, phosphate and organic species. Copper mobility may also be reduced by the formation of sulfides.

Sulfides play an important role in limiting the mobility of lead in the sediments. It is indicated that lead mobility may be facilitated by the formation of soluble lead phosphate.

The concentration of zinc in the sediment solid phase does not appear to be strongly influenced by sulfide content. Zinc mobility is increased, however, by the formation of soluble Zn-phosphate complexes.

The formation of insoluble sulfides by these metals in the anoxic sediments appears to be the most significant factor involved in limiting their mobility.

REFERENCES

Allen, B.L. and Hajek, B.F. (1989). Mineral occurrence in soil environments. In: Dixon, J.B. and Weed, S.B. (eds). *Minerals in soil environments*, 2nd edition. Soil Science Society of America, Madison.

Allen, H.E., Fu, G. and Deng, B. (1993). Analysis of Acid Volatile Sulfide (AVS) and Simultaneously Extracted Metals (SEM) for the Estimation of Potential Toxicity in Aquatic Sediments. *Environmental Toxicology and Chemistry*, **12**, 1441-1453.

Alloway, B.J. (1995a). Soil processes and the behaviour of metals, In: Alloway, B.J.(ed). *Heavy metals in soils*, 2nd edition, Blackie Academic and Professional, London.

Alloway, B.J. (1995b). Cadmium, In: Alloway, B.J. (ed). *Heavy metals in soils*, 2nd edition, Blackie Academic and Professional, London.

Baker, D.E. and Senft, J.P. (1995). Copper, In: Alloway, B.J. (ed). *Heavy metals in soils*, 2nd edition, Blackie Academic and Professional, London.

Balls, P.W. (1989). The partition of trace metals between dissolved and particulate phases in European coastal waters: a compilation of field data and comparison with laboratory studies. *Neth. J. Sea Res.*, **23**, no 1, 7-14.

Bates, R.G. (1982). pH measurements in the marine environment. *Pure and Applied Chemistry*, **54**, 229-232.

Bearman, G. (ed). (1989a). Seawater: its composition, properties and behaviour. *The Open University*. The Open University (Milton Keynes) and Pergamon Press (Oxford).

Bearman, G.(ed). (1989b). Ocean Chemistry and deep-sea sediments. *The Open University*. The Open University (Milton Keynes) and Pergamon Press (Oxford).

Berner, R.A. (1975). The role of magnesium in the crystal growth of calcite and aragonite from sea water. *Geochim. Cosmochim. Acta*, **39**, 489-504.

Boughriet, A., Ouddane, B., Fischer, J.C. Wartel, M. and Leman, G. (1992). Variability of dissolved Mn and Zn in the Seine Estuary and chemical speciation of these metals in suspended matter. *Water Research*, **26**, no.10, 1359-1378.

Brookins, D.G. (1988). *Eh-pH diagrams for geochemistry*. Springer-Verlag, Berlin.

Bufflap, S.E. and Allen, H.E. (1995). Sediment pore water collection methods for trace metal analysis: a review. *Water Research*, **29**, no.1,165-177.

Buffle, J. (1988). *Complexation reactions in aquatic systems: an analytical approach*. Ellis Horwood Limited, Chichester.

Burton, J.D. and Stratham, P.J. (1990). In: Furness, R.W. and Rainbow, P.S.(eds). *Heavy metals in the marine environment*. CRC Press, Florida.

Carter, R. (1995). *Specialist study on the effects of dredging on marine ecology and mariculture in Saldanha Bay*. Portnet Saldanha: Proposed extension of the General Cargo Quay, Appendix 2. CSIR Environmental Services.

Chester, R. (1990). *Marine Geochemistry*. Chapman and Hall, London.

Chiffoleau, J., Cossa, D., Auger, D. and Truquet, I. (1994). Trace metal distribution, partition and fluxes in the Seine estuary (France) in low discharge regime. *Marine Chemistry*, **47**, 145-158.

Clegg, S.L. and Sarmiento, J.L.(1989). The hydrolytic scavenging of metal ions by marine particulate matter. *Prog. Oceanog.*, **23**, 1-21.

Comber, S.D.W., Gunn, A.M. and Whalley, C. (1995). Comparison of the partitioning of trace metals in the Humber and Mersey Estuaries. *Marine Pollution Bulletin*, **30**, no.12, 851-860.

Cooper, D.C. and Morse, J.W. (1998a). Extractability of metal sulphide minerals in acidic solutions: application to environmental studies of trace metal contamination within anoxic sediments. *Environ. Sci. Technol.* **32**, 1076-1078.

Cooper, D.C. and Morse, J.W. (1998b). Biogeochemical controls in trace metal cycling in anoxic marine sediments. *Environ. Sci. Technol.* **32**, 327-330.

Covington, A,K and Whitfield, M. (1988). Recommendations for the determination of pH in sea water and estuarine waters. *Pure and Applied Chemistry*, **60**, 865-870.

CSIR (1995). *Proposed extension of the general cargo quay, Port of Saldanha - Draft Environmental Impact Report.* CSIR Environmental Services.

Cundy, A.B. and Croudace, I.W. (1995). Physical and chemical associations of radionucleotides and trace metals in estuarine sediments: an example from Poole Harbour, Southern England. *J. Environ. Radioactivity*, **29**, no.3, 191-211.

Davies, B.E. (1995). Lead, In: Alloway, B.J. (ed), *Heavy metals in soils*, 2nd edition, Blackie Academic and Professional, London.

De Groot, A. (1995). Metals and sediments: a global perspective, In: Allen, H.E. (ed). *Metal contaminated aquatic sediments*, Ann Arbor Press, Michigan.

De la Cruz, M.A. (1978). Marine geophysical and geological investigations in Saldanha Bay. *Marine Geoscience Group, Bulletin no.9*, Joint Geological Survey / University of Cape Town.

Di Toro, D.M., Mahony, J.D., Hansen, D.J., Scott, K.J., Hicks, M.B., Mayr, S.M and Redmond, M.S. (1990). Toxicity of cadmium in sediments: the role of acid volatile sulphide. *Environmental Toxicology and Chemistry*, **9**, 1487-1502.

Drever, J.I. (1997).*The geochemistry of natural waters - surface and groundwater environments, 3rd* edition. Prentice Hall Publishers.

Dzombak, D.A. and Morel, F.M.M. (1990). *Surface Complexation Modelling – Hydrous Ferric Oxide*. John Wiley and Sons, New York.

Ebbing, D.D. (1987). *General Chemistry*, 2nd edition. Houghton Mifflin Company, Boston.

Ekpo, B.O. and Ibok, U.J. (1998). Seasonal variation and partition of trace metals (Fe, Zn, Cu, Mn, Cr, Cd and Pb) in surface sediments: relationship with physico-chemical variables of water from the Calabar River, South Eastern Nigeria. *Environmental Geochemistry and Health*, **20**, 113-121.

Flemming, B.W. (1977). Depositional processes in Saldanha Bay and Langebaan Lagoon. *Marine Geoscience Group, Bulletin no.8*, Joint Geological Survey / University of Cape Town.

Förstner, U. and Wittmann, G.T.W. (1979). *Metal pollution in the aquatic environment.* Springer-Verlag, Berlin.

Fu, G., Allen, H.E. and Cao, Y. (1992). The importance of humic acids to proton and cadmium binding in sediments. *Environmental Toxicology and Chemistry*, **11**, 1363-1372.

Furness, R.W. and Rainbow, P.S. (eds). (1990). *Heavy metals in the marine environment.* CRC Press, Florida.

Gardner, B.D., Connell, A.D., Eagle, G.A., Moldan, A.G.S. and Watling, R.J. (1985). *South African Marine Pollution Survey Report 1979-1982.* South African National Scientific Programmes Report No. 115.

Grasshoff, K., Ehrhardt, M. and Kremling, K. (eds). (1983). *Methods of seawater analysis*, 2nd edition. Verlag Chemie, Weinheim.

Hall, G.E.M., Vaive, J.E., Beer, R. and Hoashi, M. (1996). Selective leaches revisited, with emphasis on the amorphous Fe oxyhydroxide phase extraction. *Journal of Geochemical Exploration,* **56**, 59-78.

Honeyman, B.D. and Santschi, P.H. (1992). The role of particles and colloids in the transport of radionucleotides and trace metals in the oceans. In: Buffle, J. and van Leeuwen, H.P. (eds). *Environmental Particles* vol.1.

Horowitz, A.J. (1991). *A primer on sediment - trace element chemistry*, 2nd edition. Lewis Publishers, Michigan.

Ingersoll, C.G., Dillon, T. and Biddinger, G.R. (eds), (1997). *Ecological risk assessment of contaminated sediments.* SETAC Press, Florida.

Janssen, R.P.T., Pretorius, P.J., Peijnenburg, W.J.G.M., van den Hoop, M.A.G.T. (1996). *Determination of field based partition coefficients for heavy metals in Dutch soils and the relationship of these coefficients with soil characteristics.* RIVM report 719101023, Bilthoven, the Netherlands.

JCPDS, (1980). *Mineral Powder Diffraction File*, Search Manual.

Johnston, R.J. (1991). *Multivariate statistical analysis in geography: a primer on the general linear model.* Longman Scientific and Technical, New York.

Jones, B.R. and Laslett, R.E. (1994). Methods for analysis of trace metals in marine and other samples. *Aquatic Environment Protection: Analytical Methods*

No 11. Directorate of Fisheries Research, Ministry for Agriculture, Food and Fisheries. UK.

Kiekens, L. (1995). Zinc. In: *Heavy metals in soils*, 2nd edition. Alloway, B.J. (ed). Blackie Academic and Professional.

King, C.A.M. (1974). *Introduction to marine geology and geomorphology*. Edward Arnold, London.

Kirkwood, D.S. (1994). The SAN^{plus} segmented flow analyser. *Seawater analysis.* Publication No 07300194. Ministry of Agriculture, Fisheries and Food (MAFF). Lowesoft, UK.

Knesl, O. (1996). *A geochemical investigation of the waters and sediments of Barber's Pan, North West Province*. M.Sc. Thesis, University of Cape Town.

Lanz, J. (1997). *A geochemical investigation of the waters and sediments of de Hoop Vlei, Bredasdorp District, South Africa.* M.Sc. Thesis, University of Cape Town.

Lee, S.Z., Allen, H.E., Huang, C.P., Sparks, C.P., Sanders, P.F. and Peijnenburg, W.J.G.M. (1996). Predicting soil-water partition coefficients for cadmium. *Environmental Science and Technology*, **12**, 3418-3424.

Libes, S.M. (1992). *An Introduction to Marine Biogeochemistry*. John Wiley and Sons, Inc., New York.

Luoma, S.N. (1986). A comparison of two methods for determining copper partitioning in oxidised sediments, *Marine chemistry*, **20**, 45-59.

Luoma, S.N. and Bryan, G.W. (1981). A statistical assessment of the form of trace metals in oxidised estuarine sediments employing chemical extractants. *Sci. Total Environ.*, **17**, 165-196.

Luoma, S.N. and Davis, J.A. (1983). Requirements for modelling trace metal partitioning in oxidised estuarine sediments, *Marine Chemistry*, **12**, 159-181.

Luther, G.W. (1995). Trace metal chemistry in porewaters, In; *Metal contaminated aquatic sediments*, Allen, H.E. (Ed). Ann Arbor Press, Michigan.

Magnusson, B. and Westerlund, S. (1981). Solvent extraction procedures combined with back-extraction for trace metal determinations by atomic absorption spectrophotometry. *Analytica Chimica Acta*, **131**, 63-72.

McBride, M.B. (1994). *Environmental Chemistry of Soils*. Oxford University Press.

Millero, F.J. (1996). *Chemical Oceanography*, 2nd edition. CRC Press, Florida.

Morrison, G.M.P., Batley, G.E. and Florence, T.M. (1989). Metal speciation and toxicity. *Chemistry in Britain*, August 1989, 791-796.

Morse, J.W. (1995). Dynamics of trace metal interactions with authigenic sulphide minerals in anoxic sediments, In; *Metal contaminated aquatic sediments*, Allen, H.E. (ed). Ann Arbor Press, Michigan.

Morse, J.W. (1986). The surface chemistry of calcium carbonate minerals in natural waters: An overview. *Marine Chemistry*, **20**, 91-112.

Murray, K. and Wade, P. (1996). Checking anion-cation balance of water quality analyses: limitations of the traditional method for non-potable waters. *Water SA*, **22**, 27-32.

Ng, B., Turner, A., Tyler, A.O., Falconer, R.A., and Millward, G.E. (1996). Modelling contaminant geochemistry in estuaries. *Water Research*, **30**, no.1, 63-74.

Oakley, S.M., Nelson, P.O. and Williamson, K.J. (1981). Model of trace metal partitioning in marine sediments. *Environmental Science and Technology*, **15**, 474-480.

Pardue, J.H. and Patrick, W.H. (1995). Changes in metal speciation following alteration of sediment redox status. In: Allen, H.E. (ed). *Metal contaminated aquatic sediments*, Ann Arbor Press, Michigan.

Pough, F.H. (1987). *A field guide to rocks and minerals – Peterson field guides (no.7)*. Houghton Mifflin Company, New York.

Pretorius, P.J., Janssen, R.P.T., Peijnenburg, W.J.G.M. and van den Hoop, M.A.G.T. (1996). *Chemical equilibrium modelling of metal partitioning in soils*, Report no. 719101024, National Institute of Public Health and the Environment, Bilthoven, The Netherlands.

Pretorius, P.J. (1997). *The adsorption of Ni, Cu, Zn, Cd and Pb by δ-MnO_2 and its inclusion in an equilibrium model of metal partitioning in soils*. PhD Thesis, University of Cape Town.

Radovanovic, H. and Koelmans, A. (1998). Prediction of *in situ* trace metal distribution coefficients for suspended solids in natural waters. *Environmental Science and Technology*, **32**, 753-759.

Reeburgh, W.S. (1967). An improved interstitial water sampler, *Limnology and Oceanography*, **12**, 163-165.

Regnier, P. and Wollast, R. (1993). Distribution of trace metals in suspended matter of the Scheldt estuary, *Marine Chemistry*, **43**, 3-19.

Schlautman, M.A. and Morgan, J.J. (1994). Adsorption of aquatic humic substances on colloidal-size aluminium oxide particles: influence of solution chemistry. *Geochimica et Cosmochimica Acta*, **58**, no.20, 4293-4303.

Shannon, L.V. and Stander, G.H. (1977). Physical and chemical characteristics of water in Saldanha Bay and Langebaan Lagoon. *Transactions of the Royal Society of South Africa*, **42**, parts 3 and 4, 441-460.

Shea, D. (1988). Developing national sediment quality criteria. *Environmental Science and Technology*, **22**, 1256-1261.

Shriver, D.F., Atkins, P.W. and Langford, C.H. (1990). *Inorganic Chemistry*. Oxford University Press, Oxford.

Sirinawin, W., Turner, D.R., Westerlund, S. and Kanatharana, P. (1998). Trace metals study in the Outer Songkla Lake, Thale Sap Songkla, a southern Thai estuary. *Marine Chemistry*, **62**, 175-183.

Sposito, G. (1989). The chemistry of soils. Oxford University Press, New York.

Standard Methods. (1995). *Standard methods for the examination of water and wastewater*, 19th edition. American Public Health Association; American Water Works; Water Environment Federation, Washington DC.

Stumm, W. (1992). *Chemistry of the solid-water interface : processes at the mineral-water and particle-water interface in natural systems*. John Wiley and Sons, New York.

Sung, W. (1995). Some observations on surface partitioning of Cd, Cu and Zn in estuaries. *Environmental Science and Technology*, **29**, no.5, 1303-1312.

Technicon Corporation (1969). Sulfate in water and wastewater. *Industrial Method, 39-69W*.

Tessier, A. and Campbell, G.C. (1988). Partitioning of trace metals in sediments, In: Kramer, J.R. and Allen, H.E. (eds). *Metal Speciation: Theory, Analysis and Application*. Lewis Publishers, p.182-199.

Theron, A.K. (1995). *Specialist study on the potential physical impacts of the proposed port development on the Saldanha Bay beaches.* Portnet Saldanha: Proposed extension of the General Cargo Quay, Appendix 5. CSIR Environmental Services.

Valenta, P., Duursma, E.K., Merks, A.G.A., Rützel, H. and Nürnberg, H.W., (1986). Distribution of Cd, Pb and Cu between the dissolved and particulate phase in the Eastern Scheldt and Western Scheldt estuary. *Sci. Total Environ.*, **53**, 41-76.

Van Cappellen, P. and Wang, Y. (1995). Metal cycling in surface sediments: modeling the interplay of transport and reaction. In: Allen, H.E. (ed). *Metal contaminated aquatic sediments*, Ann Arbor Press, Michigan.

Van den Hoop, M.A.G.T. (1995). *Metal speciation in Dutch soils: Field based partition coefficients for heavy metals at background levels.* Dutch Institute of Public Health and the Environment report no. 719101013, Bilthoven, the Netherlands.

Wedepohl, K.H. (1971). *Geochemistry.* Holt, Rinehart and Winston Inc., U.S.A.

Wehmiller, J. (1972). Strontium: element and geochemistry. In: Fairbridge, R.W. (ed). *The Encyclopedia of Geochemistry and Environmental Sciences*, Van Nostrand Reinhold Company, New York.

Wells, M.L., Kozelka, P.B. and Bruland, K.W. (1998). The complexation of dissolved Cu, Zn, Cd and Pb by soluble and colloidal organic matter in Narragansett Bay, R.I. *Marine Chemistry*, **62**, 203-217.

Wheast, R.C. (ed). (1969). *The CRC Handbook of Chemistry and Physics*, 50th edition. The Chemical Rubber Company, Ohio.

Whittig, L.D. and Allardice, W.R. (1986). X-ray diffraction techniques. In: Klute, A. (ed). *Methods of soil analysis, Part I, physical and mineralogical methods,* 2nd edition, Soil Science Society of America, Madison.

Willis, J.P., Fortuin, H.H.G. and Eagle, G.A. (1977). A preliminary report on the geochemistry of recent sediments in Saldanha Bay and Langebaan Lagoon. *Transactions of the Royal Society of South Africa*, **42**, parts 3 and 4, 497-509.

Yen, T.F. and Tang, I.S. (1977). Chemical aspects of marine sediments, In: Yen, T.F. (ed). *Chemistry of marine sediments*. Ann Arbor Science Publishers, Michigan.

APPENDIX A

Previous studies

Physical and chemical characteristics of water in Saldanha Bay and Langebaan Lagoon (Shannon and Stander, 1977).

Table A.1 Mean values and standard deviations of physical and chemical properties of seawater at various depths for all stations combined during April 1974-October 1975. Numbers of observations in parentheses.

	Depth of water			
	0 m	5 m	10 m	20 m
Temperature (°C)	15.66±1.86(251)	14.75±1.98 (169)	13.18±1.60 (93)	11.32±1.40 (36)
Salinity (‰)	34.97±0.25 (236)	34.90±0.16 (158)	34.84±0.10 (91)	34.81±0.10 (36)
DO (mL/L)	6.02±1.30 (196)	5.57±1.14 (170)	4.79±1.08 (96)	3.59±1.26 (36)
Nitrate (mg N/m^3)	5.6±5.1 (190)	7.3±5.7 (167)	11.6±6.8 (95)	19.6±7.3 (36)
Inorg phosphate (mg P/m^3)	1.4±1.0 (191)	1.4±0.8 (168)	1.4±0.7 (95)	1.6±0.8 (36)
Total phosphate (mg P/m^3)	2.1±1.3 (181)	2.1±1.0 (158)	2.2±1.1 (86)	2.4±1.2 (31)
Silica (mg Si/m^3)	19.2±15.4 (192)	18.9±13.1 (168)	19.9±10.4 (94)	23.5±9.6 (36)
pH	8.26±0.14 (181)	8.24±0.12 (156)	8.20±0.12 (83)	8.12±0.13 (28)
COD (mg/L)	8.2±10.5 (185)	8.0±10.0 (167)	7.9±9.6 (93)	9.1±12.7 (35)
OA (mg/L)	1.7±0.9 (175)	1.6±0.9 (156)	1.5±1.0 (89)	1.2±0.6 (34)

DO: dissolved oxygen; COD: chemical oxygen demand; OA: oxygen available

APPENDIX B

Analytical appraisal (sediment solid phase analyses)

B.1 Precision

To test the precision of the metal analyses by FAAS, repeat analyses of one sample (C14) were performed. Relative standard deviations were calculated for these repeat analyses and these are presented in Table B.1. The results of the RSD calculations indicate acceptable levels of precision for the purpose of this study.

Table B.1 Relative standard deviations (RSD) calculated for repeat analyses (four repeats) of sample C14 for metals by FAAS.

FAAS analysis	RSD (%)
Al	1.07
Cd	0.93
Cu	1.03
Fe	1.07
Mn	1.05
Pb	2.36
Zn	2.77
Na	0.59
K	2.62
Mg	1.10
Ca	0.28

B.2 Accuracy

A certified reference material, PACS-2, was used during the analyses of the sediment samples for metals by FAAS. This reference material is a powdered marine sediment used for the analysis of trace metals and other constituents. It is produced by the

National Research Council of Canada. The results of these analyses indicated acceptable levels of accuracy for this analytical method.

The accuracy of the WDXRFS data was checked by the summation of all major oxides, LOI and H_2O and comparison of the sum to 100 %. All the WDXRFS analyses showed errors of less than 3 %.

Analysis of standards for acid volatile sulfides (AVS) achieved a recovery of 97 %.

APPENDIX C

Raw data for Chapter 3

Table C.1 Results of organic carbon, nitrogen and hydrogen analyses

Sample	% Organic carbon	% Nitrogen	% Hydrogen
C1	6.50	0.19	0.65
C2	0.79	0.28	0.22
C3	0.46	0.19	0.23
C4	6.90	0.39	0.48
C5	6.23	1.02	0.44
C6	3.37	0.26	0.63
C7	3.66	0.60	0.66
C8	0.84	1.35	0.19
C9	na	na	0.16
C11	1.92	0.14	0.15
C12	0.59	0.62	0.16
C13	0.31	0.34	0.14
C14	0.88	0.06	0.31

na: data not available

Table C.2 Concentrations (mg/kg) of metals extracted with hydroxylamine hydrochloride/ HCl.

Sample	Al	Fe	Mn
C1	14.6	28.8	2.12
C2	222	614	3.63
C3	221	647	3.79
C4	24.5	19.2	1.99
C5	13.4	246	2.66
C6	9.74	13.2	1.77
C7	1.38	120	2.00
C8	10.3	6.65	1.63
C9	20.5	11.2	1.64
C11	15.7	24.3	1.78
C12	1.16	7.62	1.60
C13	10.5	17.0	1.99
C14	9.90	11.2	3.20

anion-cation charge differences for the pore water samples range from 0.88 to 3.32 % and therefore the data can be considered to be of good quality. The charge balance data are presented in section 5 of chapter 4.